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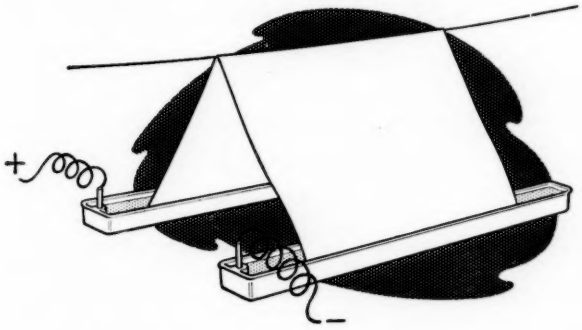
ANALYTICAL ABSTRACTS

PROGRESS IN

CHROMATOGRAPHY 2



SEPARATION OF LARGE MOLECULES BY ELECTROPHORESIS

Since most large molecules and colloidal particles carry a charge, electrophoresis is obviously a convenient method of separation. However, the disadvantage is that, when the potential gradient is merely applied across a buffered solution of the material to be separated, re-mixing may occur owing to convection currents, and complete resolution of the fractions is not possible.

Such difficulties have been overcome by using filter paper to provide a capillary mesh to hold the solution. Each end of a filter paper sheet soaked in buffer dips into a trough containing an electrode and a quantity of the buffer solution. When a solution of the test material is applied to the centre of a strip, its components will migrate towards one or other of the electrodes. Their direction and rate of travel (hence their position on the strip) will furnish a clue to their identity. Re-mixing cannot occur, and the fractions are available for both qualitative and quantitative examination.

ELECTROPHORETIC ANALYSIS OF SERUM PROTEINS IN CHRONIC RHEUMATIC DISEASES

The analysis of serum protein for purposes of diagnosis has been greatly advanced by paper electrophoresis. Kunkel and Tiselius (*J. Gen. Physiol.*, **35**: 89. 1951-2) have described a procedure which is 'extremely simple and surprisingly accurate', but lay great stress upon the importance of using the right filter paper. The reason for this is that, though human albumin migrates towards the anode, there is an electro-osmotic flow of buffer solutions towards the cathode. It has been found that Whatman 3MM. paper is satisfactory in reducing this flow to the desired minimum. The physician's diagnosis is confirmed by an increase of gamma globulin and some decrease in albumin, both of which are revealed by simple inspection. The paper strip method brings electrophoretic analysis well within the scope of normal clinical laboratory routine, and compares very favourably with previous techniques on cost, time and accuracy.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1959. **Evaluation and comparison of analytical procedures.** H. Kaiser and H. Specker (Inst. Spektrochem. u. angew. Spectroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 46–66.—Elementary error theory is discussed in this account of the applications of statistical methods to the evaluation of test procedures. Terms are defined and such expressions as standard error of the mean and confidence limits are explained. Statistical treatment of data, particularly from small samples, comparison of means and standard deviations, and investigations of sources of error are covered. Some worked examples are collected together in an appendix. B. J. WALBY

1960. **Application of statistics to the determination of sensitivity limits.** J. Domenech, F. Estalrich, C. Ochoa and J. Ribé. *Afinidad*, 1955, **32**, 103–109.—A statistical procedure, involving weighting the Gaussian error curve, is developed for calculating the sensitivities of a test method, *i.e.*, the concn. limits to give 1, 50 or 99 per cent. of positive results. The procedure is applied to the electrophoretic detection of Pb and Ni. L. A. O'NEILL

1961. **Fluoroberyllates in chemical analysis.** A. K. Ghosh and A. B. Ray (Presidency Coll., Calcutta, India). *Anal. Chim. Acta*, 1956, **14** (2), 112–114.—Barium (70 mg) can be separated quant. from Pb^{++} (700 mg) by pptg. $BaBeF_4$ in the presence of EDTA. *Procedure*—To an acid soln. containing 27 to 70 mg of Ba^{++} add 10 ml of 10 per cent. EDTA (disodium salt) soln. and adjust to pH 6 with dil. aq. NH_3. Heat to boiling point and add 10 ml of 10 per cent. ammonium fluoroberyllate soln. dropwise, with stirring. Keep the soln. hot for a few min., cool to room temp., filter in a sintered-glass crucible, wash the ppt. with cold water, dry at 110° C and weigh. W. C. JOHNSON

1962. **The continuous extraction of mixtures with any desired mode of parameter change according to the principle of diagram testing.** R. K. Zahn and I. Stahl (Inst. für veg. Physiol, J. W. Goethe Univ., Frankfurt, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (4–6), 204–216.—An apparatus is described by which adsorption on a suitable medium is allowed to take place and the subsequent elution can be carried out under conditions which permit any desired variation in the composition and rate of flow of the eluting liquid. Details are given for constructing the diagram by which the actual separation is followed, and an example of the operation of the apparatus in the separation of the proteins of human serum is given. Seven distinct protein fractions were recognised. F. POWELL

1963. **Spot analysis. XXI–XXVII.** Isamu Tsubaki and Shigeo Hara (Osaka Ind. Tech. Res. Inst., Saida-cho, Ikeda, Osaka). *Japan Analyst*, 1955, **4** (9), 563–565.—The following methods of detection were studied. (*i*)—Uranous ions (>0·98 μg) are oxidised with ferric iron and the Fe^{++} obtained are detected with dimethylglyoxime in an ammoniacal soln. containing tartrate. (*ii*)—Carbonate ions decolorise the brown soln. resulting from uranyl acetate and ferrocyanide. This reaction is applied to the detection of CO_3'' (> 0·4 μg) in the absence of phosphoric acid. (*iii*)—Selenium (> 10 μg) is detected by adding one drop of the sample soln. in 5 per cent. KCN to HCl (1 + 1). (*iv*)—Cadmium (> 0·7 μg) is detected on a micro scale with an HNO_3 soln. (1 + 100) of cinchonine (1 per cent.) and KI (2 per cent.). (*v*)—Bromide ions (> 5 μg) are detected, in the presence of Cl′, with an HNO_3 soln. (≃ 0·8 *N*) of $Bi(NO_3)_3$ (5 per cent.) and cinchonine chloride (1·6 per cent.). (*vi*)—Germanium (> 5 μg) is pptd. in an elementary state with vanadous soln., produced by the reduction of a saturated aq. soln. of ammonium metavanadate with zinc amalgam. (*vii*)—Beryllium (> 3 μg) is detected by its antagonism to the masking of the yellow colour produced from $Ti(SO_4)_2$ (1 per cent.) and H_2O_2 (3 per cent.) by F′ (1 per cent. KF). K. SAITO

1964. **The application of thiosalts in analysis. IV. A new scheme of qualitative analysis. Part B. Insoluble substances in qualitative analysis.** G. B. S. Salaria (Mahendra College, Patiala, India). *Anal. Chim. Acta*, 1956, **14** (2), 97–99.—A scheme is given for the identification of substances that remain undissolved when the sample is treated with acid, as described in Part A (*cf. Anal. Abstr.*, 1956, **3**, 1599). W. C. JOHNSON

1965. **Use of chloramine T in qualitative analysis.** E. G. Maleeva (Stalin Technol. Inst., Odessa). *Zhur. Anal. Khim.*, 1955, **10** (6), 380–381.—Chloramine T can be used as an oxidation agent in place of chlorine water, for example in the oxidation of Cr^{III} to CrO_4'' in alkaline soln., oxidation of Mn^{II} to Mn^{IV} in alkaline soln., oxidation of Fe^{II} to Fe^{III} in alkaline soln., and dissolution of NiS and CoS in dil. HCl. G. S. SMITH

1966. **Use of the benzyldimethylphenylammonium ion as a group anion reagent.** K. B. Yatsimirskiĭ and Z. I. Blagoveshchenskaya. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 90–93; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,391.—Benzyldimethylphenylammonium ions give ppt. with Cr_2O_7'', S_4O_6'', $[Fe(CN)_6]'''$, $[Fe(CN)_6]''''$ and I′. Limiting dilutions and minimum amounts detectable are—with S_4O_6'', 1 in 2000. 0·5 μg in a 0·001-ml drop; with $[Fe(CN)_6]'''$, 1 in 2000, 0·5 μg; with $[Fe(CN)_6]''''$ (only in acid solution), 1 in 17,000, 0·059 μg; with Cr_2O_7'', 1 in 2000, 0·36 μg; and with I′, 1 in 400, 2·5 μg. Photomicrographs of the crystals are given. G. S. SMITH

1967. **Kinetic methods of quantitative analysis. I. Theoretical bases of kinetic methods of quantitative analysis.** K. B. Yatsimirskiĭ (Ivanovo Chem.-Tech. Inst.). *Zhur. Anal. Khim.*, 1955, **10** (6), 339–343.—A theoretical analysis of the conditions under which kinetic methods can be used in quant. analysis is given. Determinations of the rates of chemical reactions can be used to find the concn. of reacting substances. If v is the rate of reaction of the substances A and B of concn. C_A and C_B, then $v = kC_A^nC_B^m$, where n and m are usually whole no. If the concn. of the reacting substances remains approx. constant during the course of the experiment, *e.g.*, as in the reaction between H_2O_2 and I′, the rate of reaction remains approx. constant. The rate is found by measuring the change in concn. of one of the products in unit time, *e.g.*, that of I. For this a graph of time - concn. can be constructed and the slope of the line determined. If C_B can be kept constant then $C_A = k'v^{1/n}$. G. S. Smith

1968. **Mixed one-colour acid - alkali indicators.** G. I. Mikhaĭlov (Sci. Res. Inst. of Chem. Reagents, Moscow). *Zhur. Anal. Khim.*, 1955, **10** (6), 382–383.—By the mixture of two suitably chosen one-colour acid - alkali indicators it is possible to obtain an indicator showing a colourless pH range between two coloured ranges. Thus when 0·1 per cent. alcoholic soln. of hexamethoxytriphenylmethanol and thymolphthalein are mixed in equal amounts the mixed indicator is red from pH 0 to 4·6, colourless from pH 4·6 to 9·3, and blue from pH 9·3 to 14. Various other examples are given. G. S. Smith

1969. **Mixed adsorption indicators in argentimetry.** I. N. Bulanzhe and G. A. Mel'nik. *Sbornik Trudov Kievsk. Tekhnol. Inst. Legk. Prom.*, 1954, (6), 74–82; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,402.—The following mixed adsorption indicators are recommended for the titration of $AgNO_3$ with KBr—rhodamine 6G and methylene blue (**I**), rhodamine 6G and fluorescein (**II**), and methylene blue and fluorescein (**III**). Methylene blue is used as a 0·1 per cent. aq. alcoholic solution, the other dyes as 0·1 per cent. alcoholic solutions. To titrate 10 to 25 ml of 0·01 to 0·001 N $AgNO_3$ with 0·01 to 0·001 N KBr, three drops of one component are added and then one to two drops of the second component. **I** and **II** are suitable at pH 1·34 to 7·0, **III** is suitable at pH 6 to 9·4. Parallel titrations agree to within 0·02 ml. The max. error is 0·04 ml. Partial extraction of the indicator occurs when *iso*butyl or *iso*amyl alcohol, $CHCl_3$ or benzene is present. **III** can be used in the presence of benzene and *iso*amyl alcohol. No interference is caused by $\not>$ 20 per cent. of $Na_2SO_4.10H_2O$, $CuSO_4.5H_2O$ and $\not>$ 3 per cent. of $Ba(NO_3)_2$. G. S. Smith

1970. **Diethylenetetra-ammonium sulphatocerate [ceric ethylenediamine sulphate] as volumetric reagent. I. Iodine monochloride method.** B. Singh and S. Singh (Panjab Univ. Coll., Hoshiarpur, India). *Anal. Chim. Acta*, 1956, **14** (2), 109–111.—The compound formulated by the authors as $[Ce(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2](SO_4)_2.2H_2SO_4.7H_2O$ (prep. described) is a stable substance and its use as a volumetric standard is proposed. A 0·02 N soln. in dil. H_2SO_4 is used to titrate soln. of KI, $SnCl_2.2H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$, $N_2H_4.H_2SO_4$, As_2O_3, TlCl, $K_4Fe(CN)_6$ and quinol. *Procedure*—Dissolve the weighed sample in 25 ml of water and 50 ml of conc. HCl and add 5 ml of 0·01 M ICl and 5 ml of $CHCl_3$. Cool to room temp. and titrate with a 0·02 N soln. of the reagent. Shake the flask vigorously when approaching the end-point, which is marked by a change from pale violet to very pale yellow in the $CHCl_3$ layer. The HCl concn. must be kept between 5 N and 7 N. W. C. Johnson

1971. **Velocity barrier to eliminate absorption of carbon dioxide during titrimetric procedures.** A. M. Crestfield (Univ. Calif. Sch. Med., Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 117–118.—The micro-determination of solutions of low buffer capacity (0·3 μ-equiv. per pH unit) necessitates complete exclusion of basic and acidic vapours from the laboratory atmosphere. A simple device is described consisting of a flattened conical Lucite nozzle, the narrow end of which connects to the supply of N, whilst the other end is a semicircular plane having countersunk into it the titration vessel (for 2-ml samples). A stream of N is forced across the top of the titration vessel (at 5 to 8 cu. ft. per hr.) so that a barrier is formed through which interfering vapours cannot pass. The efficiency of the technique is shown by the fact that a soln. adjusted to pH 8·0 without barrier protection rose to pH 7·1 within 4 min. owing to absorption of CO_2, whereas, with barrier protection, no change in pH was observed. D. G. Higgs

1972. **Factors influencing the flow of current in precipitation titrations with ferrocyanide according to the dead-stop procedure.** H. L. Kies and T. S. Hien (Anal. Chem. Lab., Tech. Hoogsch., Delft, Holland). *Z. anal. Chem.*, 1955, **148** (2), 91–98.—The course of a simple potentiometric titration, in which $K_4Fe(CN)_6$ is used, is followed mathematically, and the titration error is expressed in terms of several parameters. The titration error is shown to be reduced (*a*) by working in a small vol., (*b*) by the addition of alcohol to lower the solubility product, and (*c*) by having a high concn. of $K_3Fe(CN)_6$ present. J. H. Waton

1973. **Location of acid zones on paper chromatograms.** A. L. Cochrane (The Distillers Co. Ltd., Yeast Res. Outstation, Menstrie, Scotland). *Analyst*, 1955, **80**, 909.—A technique is described that greatly facilitates the location of organic acid zones on paper chromatograms developed by upward displacement in ammoniacal 80 per cent. ethanol. The papers removed from the tank are notched at the edges to mark the solvent front and are allowed to dry. They are then sprayed with 0·1 per cent. bromophenol blue in 70 per cent. aq. ethanol and NH_3 vapour is blown gently on to them. They are then exposed to HCl vapour by blowing across the neck of a bottle of conc. acid. The background colour rapidly changes to yellow, but the zones containing the weakly dissociated acids act as buffers and retain the intense blue colour considerably longer. Certain weakly dissociated inorganic acids (*e.g.*, H_3PO_4 and H_3BO_3) and some amino acids behave similarly. A. O. Jones

1974. **Indicators for the paper chromatography of lipids.** H. K. Mangold, B. C. Lamp and H. Schlenk (Univ. Minnesota, Hormel Inst., Austin, Minn., U.S.A.). *J. Amer. Chem. Soc.*, 1955, **77**, 6070–6072.—Methods are described for the detection of saturated alcohols, fatty acids, esters, glycerides and unsaturated compounds on paper chromatograms. The lipids were run on No. 1 Whatman paper by an ascending technique with the solvents

tetrahydrofuran - water (3:2) or chloroform - methanol (1:3) and the lipids were detected by the following techniques. (*i*) α-*Dextrin - iodine*—The paper is sprayed with α-dextrin (*cf. J. Amer. Chem. Soc.*, 1949, **71**, 353) (1 per cent. soln. in 30 per cent. ethanol) and air-dried. After leaving the paper in a humidifier for 1 hr. it is treated with iodine vapour in a dry container. Spots of saturated alcohols, fatty acids, esters and monoglycerides remain white, whilst the corresponding unsaturated compounds are, at first, white, then become yellow or brown; the background is violet; 20 μg can be detected. (*ii*) *Pancreatin*—Di- and tri-glycerides can be detected by the technique described above after spraying the paper with 1 per cent. aq. pancreatin soln. and incubating for 24 hr. at 37° C in a moisture chamber; 200 μg can be detected. (*iii*) *Iodine*—Unsaturated compounds can be detected by exposure to iodine vapour, when they give yellow or brown spots on a white background. Less than 20 μg can be detected. (*iv*) *Lead tetra-acetate*—If the air-dried papers are sprayed with 1 per cent. lead tetra-acetate soln. in benzene the lipids show up as white spots on a brown background; 50 to 100 μg of monoglycerides can be detected.

C. A. SLATER

1975. **Concentration of solutes for paper chromatography.** O. F. Wiegand and A. R. Schrank (Univ. Texas, Austin, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 259.—To avoid losses of liquid and other causes of error in concentrating ≃ 2 ml of soln., paraffin-wax dikes (optionally used as wicks) can be constructed to contain and concentrate the soln. of crude extracts directly on the chromatographic paper. Aliquots of 50 to 100 μl can be deposited at once in the area normally occupied by 5 μl. Alternatively, the soln. can be transferred from a bent micro-pipette on to the paper by capillarity.

W. J. BAKER

1976. **Use of helium as the mobile phase in gas chromatography.** W. A. Wiseman (Gilbey House, Oval Rd., London). *Chem. & Ind.*, 1956, (7), 127–129.—A discussion, with practical details and results, of the use of He as the mobile phase in vapour-phase chromatography is presented. A modified Phillips' apparatus (*J. Chem. Soc.*, 1955, 1480) is used, with glycerol as the stationary phase in a column 300 cm by 6 mm, and a retention time of ≃ 3·5 min. The detector is a glass catharometer combined with a 1·8-mV ether-pyrometer; all inward leaks before the detector must be eliminated. Helium provides greater sensitivity, especially at higher temp. (90° to 110° C), than does N, but with broader peaks and less resolving power. Relative retention times are approx. the same. It is preferable to N when detecting traces of methanol in ethanol.

W. J. BAKER

1977. **Trace components by sorption and vaporisation in mass spectrometry.** S. Meyerson (Standard Oil Co., Whiting, Indiana, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 317–318.—The introduction of samples into a mass spectrometer often causes changes of composition due to sorption and vaporisation and interferes with quant. analysis. By using a brass sample-introduction system these changes are readily apparent and can be used to detect, identify and determine minor components which differ from the principal component in behaviour. This technique has been used to evaluate pure compounds for use as reference spectra.

K. A. PROCTOR

1978. **Mass-spectrometric analysis. Broad applicability to chemical research.** F. W. McLafferty (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 306–316.—The use of the heated-inlet mass spectrometer is described for general qual. and quant. analysis. Applications to the positive identification of unknown components of complex mixtures, and to the determination of molecular structure, are illustrated.

K. A. PROCTOR

See also Abstract 2061.

2.—INORGANIC ANALYSIS

1979. **Transformation of heavy-metal sulphides into the soluble state by the powder-grinding method.** P. M. Isakov. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 94–100; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,399.—Natural HgS ground with I rapidly forms HgI_2. Further grinding with KI yields sol. K_2HgI_4. For qual. detection of Hg in a sample a small amount is evaporated with 1 or 2 drops of H_2SO_4 in a crucible and the residue is ground with KI. The colour changes from yellow - orange to red - orange. For determining Hg, 0·5 to 3·0 g of sample, depending on the intensity of colour obtained, are ground with I and the mixture is heated after 30 to 40 min. to complete the decomp. of HgS and to remove I. The mixture is then ground with KI. The mixture is washed into a beaker and the insol. matter is filtered off and washed with water. The Hg in the filtrate is determined as sulphide.

G. S. SMITH

1980. **Determinations with EDTA (disodium salt) in the presence of ferro - ferricyanide and benzidine as indicators.** I. Sajó (Iron Ind. Res. Inst., Budapest). *Magyar Kém. Foly.*, 1956, **62** (2), 56–59.—The author's method (*Anal. Abstr.*, 1955, **2**, 1474) has been extended to some other metals. *Procedure*—Complex the metal by adding an excess of EDTA (disodium salt) (**I**). Neutralise the soln. to phenolphthalein (if the complex is stable above pH 7), or pentamethoxytriphenylmethanol or Metanil yellow (if the complex is decomposed above pH 7). Add a buffer soln., containing ammonium acetate (500 g) and acetic acid (20 ml) in H_2O (1 litre), followed by a ferro - ferricyanide soln. [1 ml, freshly prepared from 25 ml of 1 per cent. $K_3Fe(CN)_6$ and 5 ml of 1 per cent. $K_4Fe(CN)_6$ and diluted to 100 ml] and benzidine (1 ml of a soln. of 1 g of benzidine in 100 ml of acetic acid) as indicator. The excess of **I** is back-titrated with 0·05 *N* Zn acetate, containing a little acetic acid. By varying the proportion of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, the redox potential can be varied within a range of 80 mV, permitting the use of various redox indicators. A complex is formed by V^{V} and Cr^{III} with **I** only on boiling, but Sn^{IV}, Tl^{III}, Th, Zr, La, Ce, Mo, Cu, Ni, Cd, Zn, Co^{III} and Ti react in the cold. Bivalent Co must be oxidised to Co^{III} by boiling the buffered soln. for 3 min. with 30 per cent. H_2O_2; Mn is titrated in a 40 per cent. alcoholic soln. To titrate mixtures of these metals, a reagent is added which forms a more stable complex with the metal than **I**; thus **I** is liberated and can be titrated again with Zn acetate. This can be repeated for a series of metals. The complexing agents recommended are—NaF for Al, Th, Zr, La and Ce; $NaHSO_3$ for Tl^{III}; H_2SO_4 for Pb; NH_4F or NaF for Sn^{IV}; and mannitol for Mo.

A. G. PETO

1981. **Analytical studies on phosphates. I. Amperometric titration curves of metal ions with sodium triphosphate.** Masamitsu Kobayashi (Fac. Sci., Kobe Univ., Higashinada-ku, Kobe). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (7), 793–796.—The amperometric titration of metal ions with sodium triphosphate is theoretically discussed from the viewpoints of complex formation and use for quantitative analysis. The curves can be classified into three groups: pptn., dissolution of the ppt., and complex formation. For some heavy metals, including Zn, Ni and Pb, the composition of the complex anion can be determined by the measurement of polarograms of binary mixtures of various molar ratios at several pH values.

II. Amperometric titration curves of nickel with sodium triphosphate. Masamitsu Kobayashi. *Ibid.*, 1955, **76** (7), 796–799.—Complex formation between Ni and sodium triphosphate was studied by means of amperometric titration in acetate buffer soln. within the pH range 0·8 to 7·5. The higher the pH the more stable is the anionic complex $[NiP_3O_{10}]^{'''}$. From a conc. soln., insol. needle-like crystals of $Na_3NiP_3O_{10}.12H_2O$ and fine crystals of $NaNi_2P_3O_{10}$ are obtained. For the amperometric determination of Ni, satisfactory results are obtained when the titration is carried out at pH 7·5 with a potential difference of $-1{\cdot}25$ to $-1{\cdot}4$ V *vs.* the S.C.E.

III. Amperometric titration curves of lead with sodium triphosphate. Masamitsu Kobayashi. *Ibid.*, 1955, **76** (7), 799–801.—A similar experiment was carried out with lead. The complex formation is more marked at a pH value higher than 3·5. For the determination of Pb, the titration should be carried out at pH 6·5 with a potential difference of $-0{\cdot}6$ to $-0{\cdot}7$ V.

IV. Amperometric titration curves of cadmium with sodium triphosphate. Masamitsu Kobayashi. *Ibid.*, 1955, **76** (9), 1023–1025.—A similar experiment was carried out with Cd. At a lower pH value, $NaCd_2P_3O_{10}$ is pptd., which on a further addition of sodium triphosphate dissolves to produce $Na_3CdP_3O_{10}$. K. SAITO

1982. **Use of ammonium salts in analytical chemistry. [Detection of iron, manganese and copper.]** A. Kh. Batalin and P. A. Shifrin (*Vestnik Khim. Obshch. im. D. I. Mendeleeva, Chkalovskoe Otd.*, 1954, (5), 27–30; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,387.—Certain peculiarities of dissolution of heavy-metal hydroxides and ferrocyanides in conc. solutions of ammonium salts in the presence of NaOH are studied. To separate and detect $Fe^{...}$ in the presence of $Cu^{..}$, $Mn^{..}$, $Cd^{..}$, $Bi^{...}$, $Ni^{..}$, $Co^{..}$, $Pb^{..}$, $Cr^{...}$ and $Al^{...}$, the solution is treated with excess of $K_4Fe(CN)_6$ followed by excess of conc. ammonium chloride or nitrate solution and then by excess of 10 per cent. NaOH solution. Only Fe and some of the Mn is pptd. Some of the solution is filtered and the ppt. is treated with a few drops of HCl to give Prussian blue, which indicates the presence of Fe. To separate $Mn^{..}$, the mixture of cations is treated with excess of NH_4Cl and excess of NaOH and the solution is filtered quickly. After 5 to 10 min. a ppt. of MnO_2 appears in the filtrate; Mn is identified by means of one of the usual methods. To detect $Cu^{..}$ in the presence of $Fe^{...}$, the solution is treated with $K_4Fe(CN)_6$, an excess of $NH_4^{\cdot}$ and an excess of NaOH. The ppt. contains $Fe(OH)_3$ and the solution is coloured blue from $[Cu(NH_3)_4]^{..}$. G. S. SMITH

1983. **The use of nicotine in the paper-chromatographic separation of some heavy-metal ions.** P. Szarvas, T. Balogh and B. Tóth (Kossuth Lajos Sci. Univ., Debrecen, Hungary). *Magyar Kém. Foly.*, 1956, **62** (2), 68–71.—Five metals can be separated on a paper chromatogram with acetone - conc. HCl - H_2O (85:10:5, by vol.) as solvent. The developer is nicotine - NH_4SCN (**I**) (60 g of NH_4SCN in 40 ml of water; 5 g of nicotine are added to 95 g of this soln.) or nicotine - $K_4Fe(CN)_6$ (**II**) containing 5 per cent. $K_4Fe(CN)_6$ (30 ml) and nicotine (4 g). On S. & S. No. 62 paper, with the ascending method, the R_F values are as follows [the sensitivities (μg per 0·01 ml) with **I** and **II**, respectively, are given in brackets]—Fe^{III}, 1·00 (0·01, 0·01); Cu^{II}, 0·87 (0·5, 0·1); Co^{II}, 0·66 (0·5, 0·05); Ti^{IV}, 0·29 (0·05, 0·05); Ni^{II}, 0·14 (10, 10). By using a comparative chromatogram, Cu^{II}, Co^{II} and Ni^{II} can be determined semi-quantitatively. The accuracy is $\simeq \pm 20$ per cent. A. G. PETO

1984. **Determination of hydrogen by beta-ray absorption.** R. B. Jacobs, L. G. Lewis and F. J. Piehl (Standard Oil Co., Whiting, Indiana, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 324–327.—An instrument which has given satisfactory performance with hydrocarbons in the petroleum field is described for the determination of hydrogen by measuring the β-ray absorption. The accuracy of the instrument is limited by the necessity of applying corrections for elements other than H and C. Because two opposing beams are employed, intensities do not affect the calibration and a sample may be analysed in <20 min. Four calibrations with hydrocarbons of known composition are necessary before the instrument can be used for routine work. Replicate determinations on six hydrocarbons showed a standard deviation of $\pm$ 0·03 per cent. of hydrogen. K. A. PROCTOR

1985. **Gas-counting techniques in biochemistry. I. Combustion of labelled compounds and the gas counting of carbon-14; II. Determination of tritium and some applications of gas counting to biochemical research.** R. F. Glascock (Nat. Inst. Res. Dairying, Reading Univ., England). *Atomics*, 1955, **6** (11), 329–334, 343; (12), 363–369.—Biological samples (about 5 mg) labelled with ^{14}C and/or ^3H are converted into $^{14}CO_2$ and ^3H_2O by mixing with CuO and combustion with 2 mm pressure of O at 700° C; S, the halogens and oxides of N are held back by appropriate solid absorbents. Carbon dioxide, labelled with ^{14}C, and freed from ^3H_2O by activated charcoal, is mixed with 10 per cent. v/v of CS_2 and used as the gas filling in a Geiger counter at 22 cm total pressure; the counter is operated at $\gtrsim$ 4000 V with an auxiliary quenching circuit. The ^3H_2O is converted into $^3H{\cdot}CH_2{\cdot}C_3H_7$ with *n*-butylmagnesium bromide and used as a self-quenching gas filling in a Geiger counter at 12·5 cm and about 2600 V. The efficiency of gas counting is about 80 per cent. for ^{14}C and for ^3H. E. N. JENKINS

1986. **The determination of tritium in tritiated water.** A. Finkelstein and H. Lesimple (Commissariat á l'Energie Atomique, Fort de Chatillon, France). *J. Nuclear Energy*, 1955, **2** (2), 101–109.—Samples (0·1 to 2·5 ml) of tritiated water were converted by CaC_2 into tritioacetylene which was condensed at $-$ 195° C and used to fill a 1800-ml ionisation chamber together with normal acetylene to a pressure of 5 cm; argon was also introduced to a further 3 to 5 cm. The ionisation current (10^{-12}

to 10^{-10} amp.) was measured at 230 V applied potential. The ratio of ^3H to normal H was 3 per cent. low owing to isotopic depletion during the reaction with the carbide. E. N. JENKINS

1987. **Qualitative and quantitative analysis of the alkali metals by paper electrophoresis.** O. Schier (Tech. Hochsch. Vienna, Austria). *Angew. Chem.*, 1956, **68** (2), 63–66.—It was found possible to separate Li^+, Na^+, K^+, Mg^{++}, and, together, Cs^+ plus Rb^+, from mixtures of their ions by paper electrophoresis with ammonium carbonate solution. At the end of the run this is removed by volatilisation and the paper is sprayed with an indicator to develop the chromatogram. Since the carbonates of many metals are insoluble, little interference is encountered, but interference due to Co, Cu, Ni, Hg, Ag and Th is overcome by spraying with ammonium sulphide solution, whilst any strong organic bases which may be present are removed by volatilisation. Only 10 to 50 μg are required for qualitative analysis. Quantities of 100 to 1000 μg of each metal can be estimated quantitatively by micro methods or by estimating the size of the spot. The separation requires two to three hours.

P. S. STROSS

1988. **Determination of alkali metals in meteorites by a distillation process.** G. Edwards and H. C. Utey (Inst. Nucl. Studies, Univ. Chicago, Ill., U.S.A.). *Geochim. et Cosmochim. Acta*, 1955, **7** (3–4), 154–168.—The method is based on the volatilisation of chlorides from silicates in an induction-heated crucible within a water-cooled "Vicor" jacket. The powdered meteorite (1 g) is mixed with $CaCl_2$ (0·25 g) and heated in a graphite crucible at 1300° to 1350° C for 40 min. and then at 1400° to 1450° C for 15 min., while a current of N is passed through the apparatus. The volatile chlorides condense on the jacket and are washed off and determined by flame photometry. The consistency of recovery of Na and K from silicates initially containing <1 per cent. and 0·1 per cent., respectively, is ± 3 per cent. It is concluded that the wet chemical method gives erroneous results.

N. E.

1989. **Effect of alkali and alkali-earth chlorides on the anode temperature of the d.c. arc.** B. L. Vallee and R. E. Thiers (Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (2), 83–86.—The temperature of the anode in a d.c. arc with graphite electrodes is shown to depend not only on the gas surrounding the arc but also on the sample with which the electrode is loaded. In helium the anode temperature is related to the boiling point and excitation potential of the sample, but this does not apply with an argon atmosphere. The magnitude of these temperature variations is adequate to account for the variability associated with the use of the d.c. arc in spectrochemical analysis and demonstrates the need for the use of spectroscopic buffers. B. S. COOPER

1990. **Quantitative emission spectrum analysis by solution excitation. I. Spectrographic determination of sodium in the silumin alloys.** Chiyujiyo Matsumoto, Yoshichika Oto and Takanobu Hamaguchi. *Rep. Ind. Research Inst., Osaka Pref.*, 1955, **7** (1), 15–17. An a.c. intermittent-arc source was applied so as to secure a steady and reproducible sensitivity; the solution method was adopted with a porous-cup electrode and Cu was selected as an internal standard. A series of standard sample soln. having known contents of Na and Al were prepared, the spectral lines were photographed on the same plate and the Na in the standard metal electrode was determined by the concn. ratio method. The limit of determination of Na was 0·005 per cent. with an error of $\pm$ 8·1 per cent.

II. Spectrographic determination of lead, iron, cadmium and tin in zinc metal. Chiyujiyo Matsumoto and Yoshichika Oto. *Ibid.*, 1955, **7** (1), 18–21.—An interrupted a.c. arc source unit ignited by high-frequency spark and a quartz spectrograph were used for this study. The elements in the range of 0·1 to 0·06 per cent. were determined with errors of $\pm$ 3 to 15 per cent. CHEM. ABSTR.

1991. **Polarography of potassium tetraphenylboron in dimethylformamide.** A. F. Findeis, jun., and T. De Vries (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 209–211.—A polarographic wave of $E_{\frac{1}{2}} = -1{\cdot}55$ V *vs.* the mercury-pool electrode was obtained from a soln. of K tetraphenylboron in dimethylformamide with tetrabutylammonium iodide as the supporting electrolyte. The wave heights were proportional to concn. over the range 0·0002 to 0·0075 *M*, corresponding to 0·08 to 8·0 mg of K in the cell. Interference is caused by aq. NH_3, Rb and Cs. The precision is within 3·0 per cent. G. P. COOK

1992. **Determination of potassium sulphate in natural potassium salts by a volumetric method.** G. P. Aleksandrov and Ya. N. Shuter (Inst. Geology of Useful Minerals, Acad. Sci., Ukr. SSR). *Zavod. Lab.*, 1955, **21** (12), 1432–1433.—The powdered potassium salt (0·5 to 0·2 g) is boiled for 30 min. with 100 ml of water, and 3 per cent. $Ba(OH)_2$ solution (30 ml with sylvine, and 45 ml with kainite, langbeinite or polyhalite) is added to the boiling solution, which is then kept on a steam bath for 30 min. The next day the ppt. is filtered off and washed with cold water. A stream of CO_2 is passed through the filtrate for 15 min., the bicarbonate is decomposed by boiling for 20 min., the pptd. carbonates of the alkaline-earth metals are filtered off and washed with hot water, and the filtrate containing K_2CO_3 is titrated cold with 0·1 *N* HCl to methyl red. G. S. SMITH

1993. **The use of oxalyldihydrazide in a new reaction for the spectrophotometric micro-determination of copper.** G. Gran (Swedish Forest Products Res. Lab., Stockholm, Sweden). *Anal. Chim. Acta*, 1956, **14** (2), 150–152.—When a soln (10 ml) of Cu^{++} is treated with conc. aq. NH_3 (5 ml), saturated aq. oxalyldihydrazide soln. (4 ml) and 40 per cent. acetaldehyde soln. (10 ml) a violet colour ($\lambda_{max.} = 542$ mμ) is obtained. The reaction is highly sensitive ($\epsilon = 29{,}500$). For colour-intensity measurements the soln. is diluted to 50 ml, and a curve correlating extinction with Cu^{++} concn. indicates adherence to Beer's law in the range 0 to 60 μg of Cu^{++} per 50 ml. Formaldehyde may be used in place of acetaldehyde, but the reaction is then less sensitive. With formaldehyde the max. colour intensity is obtained at pH 5 to 10.

W. C. JOHNSON

1994. **Photometric determination of copper in aluminium and lead-tin solder with neocuproine.** J. W. Fulton and J. Hastings (Gen. Elect. Co., Pittsfield, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 174–175.—Rapid procedures are described for

the use of neocuproine (2:9-dimethyl-1:10-phenanthroline) in the determination of Cu in high-purity Al, high-silicon aluminium and Pb - Sn solders. The methods are sensitive and accurate over the range of 0·002 to 0·3 per cent. of Cu in Al, and 0·004 to 0·4 per cent. of Cu in the solders. After dissolution of the sample (0·5 g), an aliquot (≡ 0·04 to 0·2 mg of Cu) of the soln. is treated according to Gahler's procedure (*Anal. Abstr.*, 1954, **1**, 1769), the Cu^{I} - neocuproine complex formed at pH 4 to 6 being extracted with a methanol - $CHCl_3$ mixture and the extinction measured at 454 mμ, with reference to a similarly treated blank soln. Beer's law is valid for both determinations and for the calibration curve prepared with pure Cu.

W. J. BAKER

1995. **Chemical analyses by the use of catalysed or induced reactions. VII. Micro-determination of copper and cobalt by spectrophotometric measurement of the spot on paper.** Shukichi Sakuraba (Faculty of Eng., Shizuoka Univ., Oiwake, Hamamatsu). *Japan Analyst*, 1955, **4** (8), 496–499.—A filter-paper impregnated with $ZnSO_4$ soln. (3 or 5 mg of Zn per ml) is spotted successively with one drop (0·015 ml) each of $(NH_4)_2Hg(SCN)_4$ (8 g of $HgCl_2$ and 9 g of NH_4SCN in 100 ml of water) and the sample soln. (5 to 50 μg of Cu or Co per ml of 0·01 *N* H_2SO_4). Characteristic spots are formed owing to the induced co-pptn. of Cu or Co with $ZnHg(SCN)_4$. After 2 to 3 hr., the paper is dried at 110°C for 2 min. and the extinction is measured (540 mμ for Cu; 600 mμ for Co). The extinction increases reproducibly (but not linearly) with increase in the concn. of Co (or Cu) (<1·0 μg per 0·02 ml). A micro amount of Cu and Co can be determined with an average deviation of 6·5 and 4·8 per cent., respectively.

K. SAITO

1996. **Determination of copper, manganese and lead in raw materials for the production of rubber.** Z. Marczenko and I. Pacewska. *Przem. Chem.*, 1955, **11**, 253–258.—In the determination of trace amounts (0·01 to 0·001 per cent.) of Cu, Mn and Pb in accelerators, stabilisers, plasticisers (paraffin, stearin) and fillers (chalk, kaolin, lithopone and zinc white), the organic matter is decomposed by ignition (<800° C), and the residue is dissolved in HCl and made up to a standard volume. Copper is determined with sodium diethyldithiocarbamate, Mn as MnO_4', and Pb with dithizone.

A. O. JAKUBOVIC

1997. **Spectrochemical analysis with a universal source unit. III. Determination of various elements in copper alloys.** Jiro Kashima and Kazuo Yasuda (Waseda Univ., Waseda, Tokyo). *Japan Analyst*, 1955, **4** (8), 491–496.—The determination of Zn in brass and of P (0·03 to 1 per cent.), Pb (0·03 to 0·5 per cent.) and Fe (0·01 to 0·3 per cent.) in bronze was studied by using a multi-source unit. For the determination of Zn (10 to 50 per cent.), a spark-like discharge (9·5 ohms; 400 μH; 10 μF; preliminary discharge, 30 sec.; exposure, 30 sec.) (Zn 3075·9 - Cu 3063·4) provides reproducible results with an error of < 2 per cent. For the determination of trace constituents in bronze (Sn, 5 to 10 per cent.), an arc-like discharge of high sensitivity (50 ohms; 400 μH; 60 μF; preliminary discharge, 5 sec.; exposure, 10 to 30 sec.) is recommended to obtain reproducible results with an error <2 per cent.

K. SAITO

1998. **Potentiometric determination of univalent silver by potassium iodate.** M. N. Radhakrishna (Phys. Chem. Lab., Hindu Univ., Benares, India). *Z. anal. Chem.*, 1956, **148** (6), 401–402.—Univalent silver in concn. from 0·001 *M* to 0·2 *M* is titrated potentiometrically with KIO_3, a pure silver plate being used as an indicator electrode. The results are in excellent agreement with those obtained by Mohr's method.

J. H. WATON

1999. **Study in the field of bismuthometry. [Determination of silver.]** L. M. Kul'berg (*Trudy Komissii Anal. Khim. Akad. Nauk*, SSSR, 1954, **5** (8), 186–196; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,431.—Titration of Ag^{+} with $KBiI_4$ solution with quinoline as indicator can be carried out in 0·5 to 8·0 *N* HNO_3. Ethanol concn. > 60 per cent. of the original vol. make the end-point less definite. No effect on the accuracy of the method is produced by temp., large amounts of neutral salts and colloids such as starch, dextrin, agar and gelatin. Solutions of concn. 0·004 *N* can be titrated satisfactorily.

G. S. SMITH

2000. **Separation of radioactive silver-111 from pile-irradiated palladium.** F. Sicilio, M. D. Peterson and G. G. Rudolph (Thayer Veterans Admin. Hospital, Nashville, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 365–366.—The separation is carried out in a remotely controlled, shielded, glass apparatus. The Pd metal is dissolved in aqua regia and 20 mg of silver carrier as the chloride complex are added. After pptn. of AgCl by dilution, redissolving in aq. NH_3 and re-pptn., the product is recovered in aq. NH_3 solution. Yields greater than 90 per cent. were obtained, the products containing < 1 μg of Pd and no activities other than ^{111}Ag being detected.

K. A. PROCTOR

2001. **The titration of silver and iodide ions with reversible redox adsorption-indicator. II.** J. Bognár and L. Nagy (Rákosi Mátyás Polytech. Univ., Miskolc, Hungary). *Magyar Kém. Foly.*, 1956, **62** (2), 43–45.—The redox indicator Patent blue V (Azure blue S) is used for the titration of I′ or Ag^{+} soln. containing a little free I. The indicator, adsorbed on the AgI, is oxidised by the I′ or HIO, formed in the presence of a very small excess of Ag^{+}. Owing to different redox-potential relations, the indicator is not oxidised by HIO when in solution. When working with 0·1 *N* soln., if 0·1 *N* alcoholic I (1 drop) is added when Ag^{+} soln. is titrated, or 0·1 *N* KIO_3 (1 drop) when an I′ soln. is determined, the end-points agree with those of potentiometric determinations. Vigorous shaking is important. The end-point is still visible in 0·0005 *N* soln. Large amounts of foreign salts (except halides) and strong acids (*e.g.*, not more than 10 *N* H_2SO_4) do not interfere.

A. G. PETO

2002. **Gravimetric determination of gold.** C. Mahr and W. Denck (Chem. Inst., Univ. of Marburg, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 67–68.—Gold is determined as the reineckate, $AuCr(NH_3)_2(SCN)_4$. Au^{III} being first reduced by AsO_3''' to Au^{I}. The reineckate has the advantages of a favourable conversion factor and of stability to drying at 110° to 120° C. It can, moreover, be used for photometry in methyl cyanide and for nephelometry. *Procedure*—Add to the gold salt solution (50 ml) in 1 to 2 *N* HCl, 0·5 *N* Na_3AsO_3 (2 ml for each 5 to 10 mg of Au) and warm until the solution is decolorised. Add immediately a fresh

1 per cent. solution of Reinecke salt (1 to 1·5 ml for each 5 mg of Au), set aside for 5 min., and then cool rapidly. Filter, wash with warm 0·01 *N* HCl and dry at 110° to 120° C. J. P. STERN

2003. **Detection of gold, platinum and palladium.** N. A. Tananaev and A. N. Chechneva. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 101–105; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,470.—To detect Pt in a soln. containing any other ions the soln. is saturated with solid NH_4Cl, shaken energetically for 1 min., filtered and washed with half-saturated NH_4Cl. The filter is then treated with a few drops of $SnCl_2$ soln. Mere traces of $(NH_4)_2PtCl_6$ give a yellow or orange colour. To detect Au, Pt and Pd in a soln. free from non-noble metals, 5 ml are saturated with NH_4Cl and shaken for 1 to 2 min. A yellow ppt. or cloudiness of $(NH_4)_2PtCl_6$ appears. A small amount of dry dimethylglyoxime is then added and the mixture is shaken and set aside for 2 to 3 min. Palladium gives a yellow amorphous ppt. A few drops of benzidine are added; a blue colour indicates the presence of Au. To detect Au and Pt in the absence of Pd in a soln. strongly coloured because of the presence of metals such as Fe, Cr, Ni, Co and Cu, the two metals are first pptd. together and then detected separately in the solution of the ppt. To separate Au and Pt, the solution is boiled with HgS for 2 to 3 min., the excess of HgS is destroyed by addition of saturated KI soln. containing 3 to 4 drops of conc. HCl per 10 ml, and the ppt. is washed first with half-saturated KI soln. to remove HgI_4' and then with hot water to remove I'. The ppt. is dissolved in aqua regia and evaporated three times with conc. HCl. The residue is dissolved in 2 to 3 ml of water. Part of the soln. is mixed with saturated ferrous ammonium sulphate soln. to precipitate Au, and the other part is treated with NH_4Cl to precipitate Pt as $(NH_4)_2PtCl_6$.
G. S. SMITH

2004. **Acidimetric determination of beryllium.** V. K Zolotukhin. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 224–228; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,434.—The soln. to be analysed (*e.g.*, 10 ml of 0·1 *N* $BeSO_4$) is treated with 5 ml of 0·5 *N* sodium tartrate soln. and exactly neutralised to phenolphthalein with 0·1 to 0·2 *N* NaOH. Potassium fluoride soln. ($\simeq$ *N*, 5 to 7 ml) neutralised to phenolphthalein is then added and the content of Be is determined by titration with 0·1 *N* HCl. Chloride, NO_3' and SO_4'' do not interfere. The only interfering cations are those whose tartrates decompose to give difficultly soluble or only slightly dissociated fluorides.
G. S. SMITH

2005. **An absorptiometric method for the determination of beryllium in beryl.** J. B. Pollock (Geological Survey of Uganda, P.O. Box 9, Entebbe, Uganda). *Analyst*, 1956, **81**, 45–48.—The method described is based on that of Osborn *et al.* (*Brit. Abstr. C*, 1944, 106), in which the extinction of the lake formed by *p*-nitrophenylazo-orcinol with Be in NaOH soln. is measured, but neither separations nor corrections are required nor are there any interferences when assaying the Uganda beryls. The beryl sample is decomposed by fusion with NaF and subsequent fuming with H_2SO_4. The soln. is treated with tartaric acid, then made alkaline and diluted to a known vol. *p*-Nitrophenylazo-orcinol is added to an aliquot portion and the extinction relative to a blank is measured in the Spekker absorptiometer, with the tungsten-filament lamp and Kodak No. 4 green filters. The content of Be is ascertained from a calibration graph prepared with pure BeO. Copper and Zn interfere, but these are absent from Uganda beryls; they can be removed as sulphides. Interference by Fe and Mn is usually negligible. The results agree with those of the gravimetric method with EDTA (Brewer, *Brit. Abstr. C*, 1953, 52). A. O. JONES

2006. **Azo dyestuffs as organic reagents. III. Detection of magnesium with *p*-nitrophenylazo-hydroxynaphthalenesulphonic acid.** Kiyo Tsuji and Kinuko Doi (Japan Women's Univ., Takatatoyokawa-cho, Bunkyo-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (11), 1187–1189.—3-(*p*-Nitrophenylazo)-4-hydroxynaphthalenesulphonic acid (**I**) and 1-(*p*-nitrophenylazo)-2-hydroxynaphthalene-3:6-disulphonic acid (**II**) were synthesised by coupling diazotised *p*-nitroaniline with 1-naphthol-3-sulphonic acid and 2-naphthol-3:6-disulphonic acid, respectively. Both **I** and **II** (0·01 per cent. in 2 *N* NaOH) are used for a sensitive detection of Mg ($> 0{\cdot}1$ μg in 0·05 ml) in the presence of other cations, including those of Ca, Al, Zn and Sn (< 500 times the amount of the Mg). Phosphate does not interfere with the colour reaction. The presence of $Fe^{\cdots}$, $Mn^{\cdot\cdot}$ (< 20 times the amount of the Mg) and $NH_4^{\cdot}$ decreases the sensitivity. When **II** is used in an ammoniacal soln. the limit of detection is 2 μg in 0·05 ml, but NH_3 masks Ni and Co. Both reagents compare favourably with the conventional *p*-nitrophenylazo-1-naphthol, which cannot be used on filter-paper. K. SAITO

2007. **Determination of magnesium with Titan yellow.** A. Bussman (Eidg. Versuchsanst. f. Obst-, Wein- und Gartenbau, Wädenswil, Switzerland). *Z. anal. Chem.*, 1956, **148** (6), 413–427.—The effect of various ions on the colorimetric estimation of Mg with Titan yellow is investigated, and methods are sought for removing their interference. The addition of NH_2OH and KCN permits Mg to be estimated (in the range 0 to 50 μg of Mg per 50 ml) in the presence of $Mn^{\cdot\cdot}$, $Fe,^{\cdot\cdot}$ $Fe,^{\cdots}$ $Cu^{\cdot\cdot}$ and $Al^{\cdots}$ up to the following ratios—Mg:Mn (1:2), Mg:Cu (>1:20), Mg:Fe (1:20) and Mg:Al (1:3). The effect of Ca is eliminated by previous pptn. with Na oxalate from acetic acid soln., even for Mg to Ca ratios of 1:300. The interference of PO_4''', which is relatively smaller, can be compensated for by the addition of excess of PO_4''' (800 μg of P per 50 ml). In the determination, the $Mg(OH)_2$ - Titan yellow adsorption complex is stabilised by the addition of 5 ml of aq. 2 per cent. poly(vinyl alcohol) soln. with 10 per cent. of glycerol. The Titan yellow reagent is stable if kept at 0° C in the dark; 5 ml of a 0·01 per cent. soln. are used. The determination is best carried out in the presence of strong alkali, the addition of 10 ml of 2 *N* NaOH being recommended. The extinction is measured between 540 and 550 mμ after the soln. has been allowed to stand for 15 to 30 min. The method has been tried successfully on the estimation of Mg in plant ash. J. H. WATON

2008. **Use of 2-hydroxy-1-naphthaldehyde in analytical chemistry. I. Gravimetric and volumetric semi-micro determinations of magnesium.** S. I. Gusev, V. I. Kumov and A. M. Stroganova (Molotov State Med. Inst.). *Zhur. Anal. Khim.*, 1955, **10** (6), 349–354.—By adding 100 ml of ethanolic *M* 2-

hydroxy-1-naphthaldehyde (**I**) and 5 ml of 10 per cent. NH_4Cl soln. to 50 ml of 0·1 *M* $MgCl_2$, then heating to 60° C and adding 5 ml of 25 per cent. aq. NH_3, characteristic greenish-yellow crystals of a complex, $C_{22}H_{14}O_4Mg$, containing 6·633 per cent. of Mg are pptd. The complex is difficultly sol. in water (0·006 per cent. at 15°C) and ethanol (0·01 per cent. at 15° C), is insol. in ether, decomposed by *N* NaOH to give $Mg(OH)_2$, and sol. in dil. acids, being re-pptd. on neutralisation. *Gravimetric determination of Mg*—The soln. of $MgCl_2$ containing about 1 mg of Mg per ml (with carnallite, 5·6042 g are dissolved in 250 ml of water) is treated with 0·2 g of NH_4Cl, ethanol to give a 50 per cent. soln., and 0·5 ml of conc. aq. NH_3. A 2 per cent. soln. of **I** in ethanol (2 ml for each mg of Mg) is added slowly to the soln. at 60° C and the sides of the beaker are rubbed with a glass rod, if necessary, to start pptn. After 30 to 35 min. the ppt. is filtered off in a glass filtering crucible, washed with 50 per cent. ethanol soln. and dried at 125° to 130° C. *Volumetric determination of Mg*—The washed ppt. as obtained in the gravimetric procedure is dissolved in a conical flask in 40 ml of ethanol and 20 ml of 0·1 *N* HCl, methyl red indicator is added, and the excess of acid is titrated with 0·1 *N* NaOH (1 ml of 0·1 HCl ≡ 0·001215 g of Mg or 0·01833 g of the complex). With minerals containing SiO_2, Ca, Al and Fe, 0·5 to 2·5 g, according to the content of Mg, are dissolved in HCl, the insol. matter is filtered off, Al and Fe are pptd. as hydroxides, and Ca is removed as oxalate; the soln. is then evaporated to between 10 and 13 ml and the procedure given above is then followed. The method is applicable also to the determination of Mg in alloys, *e.g.*, Elektron. G. S. Smith

2009. **Spectrophotometric determination of magnesium with sodium 1-azo-2-hydroxy-3-(2:4-dimethylcarboxanilido)-naphthalene-1′-(2-hydroxybenzene-5-sulphonate).** C. K. Mann and J. H. Yoe (Univ. Virginia, Charlottesville, Va., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 202–205.—This determination of trace quant. of Mg^{++} is based on the formation of a coloured complex with the compound in the title, more correctly named 3-hydroxy-4-(2-hydroxy-5-sodium-sulphophenylazo)-2-naphtho-2′:4′-xylidide (**I**), used as a 0·4 per cent. soln. in 95 per cent. ethanol. An aq. soln. (> 5 ml) containing 0·5 to 10 μg of Mg^{++} is made just acid to phenolphthalein, buffered with 0·08 *M* borax (0·5 ml), treated with reagent soln. (5 ml) and diluted (25 ml) with ethanol (95 per cent.). The salmon-pink complex develops max. colour after 30 min. and shows two absorption peaks, one at 510 mμ and the other at 540 mμ, whereas the reagent (blue) exhibits a peak at 615 mμ (at this wavelength the complex shows no absorption). Reagent concn. must be within 20 to 40 p.p.m. and must be the same for the sample as for the standards. Measurement at 510 mμ was adopted since the reagent absorbed less at this wavelength. In practice a correction must be applied to the extinction at 510 mμ (complex plus excess of reagent) and is given by a measure of the excess of reagent alone as observed at 615 mμ. Of the 71 ions examined, 30 were found to interfere, hence it was necessary to remove, or mask, most of the interfering metal ions before the Mg^{++} could be determined. Halides, NO_3', SO_4'', PO_4''', acetates and silicates were found to interfere only when salts insol. in alcohol were formed. Most interfering ions were removed by successive $CHCl_3$ extractions at pH 7 of the metal oxinates. Separation of 50 μg of Mg^{++} from 200 μg each of Al^{+++}, Cd^{++}, Co^{++}, Cu^{++}, Fe^{+++}, Mn^{++} and Ni^{++} was effective; Zn^{++} and Cd^{++} were separated by an ion-exchange technique. The sensitivity of the test is 1 in 50,000,000; Beer's law is obeyed up to 0·2 p.p.m. of Mg^{++} and the precision range is 0·12 to 0·4 p.p.m. The reagent **I** has been applied successfully to the determination of Mg^{++} in "synthetic blood ash" solutions and to samples of limestone with good precision and accuracy. D. G. Higgs

2010. **Separation of calcium and aluminium from iron by an ion-exchange method.** O. Samuelson and B. Sjöberg (Chalmers Teckn. Högsk., Göteborg, Sweden). *Anal. Chim. Acta*, 1956, **14** (2), 121–125.—For the separation of Ca^{++}, Al^{+++} and Fe^{+++} an ion-exchange column of special design is used. A funnel at a level higher than the resin surface is connected to the bottom outlet of the column through a 3-way stop-cock, so that upward elution is possible. Dowex-2 anion-exchange resin is used in a bed 15 mm × 180 mm; the particle size is 0·2 to 0·3 mm. The resin is obtained in the citrate form by passing through it 300 ml of *M* citric acid and washing with water. The slightly acid soln. of Ca^{++}, Al^{+++} and Fe^{+++} is passed downward through the column at 2 ml per min. and the column is washed with water. The Al and Fe are retained on the column and the eluate and washings contain all the Ca. The water in the column is next displaced by upward elution with conc. HCl, and to the liquid now on top of the column is added a further 75 ml of conc. HCl. The acid is passed down through the resin; the Fe is retained and the Al is washed through with conc. HCl. Finally the Fe is recovered by elution with water and *N* HCl. The separated metals are determined by known methods. The procedure is used for the analysis of lime, when Mg and Mn are obtained in the Ca-containing fraction. W. C. Johnson

2011. **Colour reaction for zinc with methyl violet and potassium ferrocyanide.** V. I. Kuznetsov and L. S. Kozÿreva. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 86–89; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,438.—Addition of $K_4Fe(CN)_6$ to an acid soln. of Zn (> 0·5 μg per ml) containing methyl violet gives a yellow colour. To prevent interference from Cu, V, Cr and Fe the soln. is made just alkaline to litmus with *N* NaOH, the ppt. is filtered off after 15 to 20 min.; the filtrate is made acid with *N* HCl, one drop of 5 per cent. hydroxylamine soln. is added and the mixture is heated at boiling point for 10 min. The cooled soln. is mixed with one drop of dil. methyl violet soln., and if necessary dil. HCl is added dropwise to give a green - blue colour. One drop of 0·2 per cent. $K_4Fe(CN)_6.3H_2O$ soln. is then added. The min. amount of Zn detectable is 1 μg per 2 ml, and the limiting dilution is 1 in 2×10^6. For quant. determination of Zn (> 150 μg), the solution diluted to 15 ml in a 25-ml flask is neutralised to litmus with *N* NaOH and 3·5 ml are added in excess. The soln. is made up to the mark and filtered after 15 to 20 min. A 20-ml portion of the filtrate is mixed with 2·8 ml of *N* HCl (the soln. should be faintly acid to Congo red) and 0·5 ml of 5 per cent. hydroxylamine sulphate soln. and boiled. One ml of the cooled solution and 0·4 ml of water are placed in one tube and 1·4 ml of water in another similar tube. Both tubes are treated with 0·3 ml of *N* HCl and 0·2 ml of 0·01 per cent. methyl violet soln. The colours are matched, if necessary adding

1 or 2 drops of *N* NaOH to the tube containing the test solution. In a third similar tube are placed 1 ml of the test solution, 0·3 ml of *N* HCl, the same amount of *N* NaOH as was found necessary to add to the first tube, water to give a vol. of 1·7 ml, 0·2 ml of 0·01 per cent. methyl violet soln. and 0·1 ml of 0·2 per cent. $K_4Fe(CN)_6.3H_2O$. The colour is compared with a scale of standards prepared simultaneously in the same way. G. S. SMITH

2012. **Complexiметric determination of zinc and cadmium in the presence of larger quantities of iron.** H. Flaschka and R. Püschel (Nat. Res. Council, Dokki, Cairo). *Z. anal. Chem.*, 1956, **149** (3), 185–189.—In the complexiметric determination of metals (Ca, Mg, Mn and Pb), certain interfering metals (including Zn, Cd and Fe) are masked by conversion into a non-reacting cyanide complex by KCN - ascorbic acid. Zinc and Cd can be selectively returned to a titratable state by the action of formaldehyde (**I**), whereas the cyanide complexes of Fe, Cu, Ni and Co are stable to **I**. A large excess of **I** must be avoided. Metals not forming cyanide complexes, and Zn and Cd, can thus be determined successively, without interference by Fe or other metals forming stable cyanide complexes. The accuracy for about 30 mg of Cd or Zn in the presence of 130 mg of Fe is within ± 0·3 per cent., and for 1 or 10 mg of Zn and 1 or 20 mg of Pb in the presence of up to 50 and 130 mg of Fe, respectively, is within ± 0·3 per cent. *Procedure*—Neutralise any large excess of acid in the sample with aq. NaOH soln. and add ascorbic acid until the colour of Fe disappears. Add aq. NH_3 (1:1) until the colour darkens, and then up to 1 g of KCN; boil the solution, when any ppt. dissolves and the colour becomes yellowish. Cool, dilute to approx. 150 ml, mask any Al or Ti with Tiron, and add Eriochrome black T indicator and 15 ml of NH_4Cl - aq. NH_3 buffer (pH 10). To free the Cd and Zn, add 10 per cent. aq. **I** dropwise until the yellow colour changes to red, then titrate with EDTA to a blue - violet end-point. Add more **I** (red colour re-appears) and repeat the titration and addition of **I** until further addition of **I** fails to produce an immediate red colour. J. P. STERN

2013. **Determination of cadmium and zinc. Separation from other elements and each other by anion exchange.** S. Kallmann, C. G. Steele and N. Y. Chu (Ledoux & Co., 359 Alfred Ave., Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 230–233.—The separation of Cd or Zn from other metals, before their determination by usual methods, depends on the formation of negatively charged zinc and cadmium chloride complexes, which are adsorbed on a strongly basic anion-exchange resin (Dowex 1, 200 to 400 mesh, column diam. 1 cm or 1 in., treated with 0·12 *N* HCl containing 10 per cent. w/v NaCl. Under these conditions, Mn, Co, Cu, Fe, Al, Ni, Cr, Ti and alkaline- and rare-earth elements are not adsorbed by the resin. The column is eluted with 2 *N* NaOH soln. containing 2 per cent. w/v NaCl, whereby Zn is removed quant., whilst Cd is retained on the resin and can be eluted with *N* HNO_3. Tin, Sb and As are partly adsorbed but can be expelled with HBr in the presence of H_2SO_4; Pb (>100 mg) and Bi (>20 mg) should be removed before the soln. of the sample is transferred to the column. The elution of Zn, completion of which is determined with benzotriazole as indicator, is independent of the cadmium concn.
W. J. BAKER

2014. **Identification of cadmium by means of sodium thiosulphate and hydrogen peroxide.** L. G. Geĭn. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 133–135; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,444.—The neutral soln. containing only Cd is heated and saturated with $Na_2S_2O_3.5H_2O$. The cooled solution is treated dropwise with H_2O_2. A yellow ppt. of CdS appears. The min. amount of Cd detectable is 0·039 mg per ml or 1·95 μg in one drop. G. S. SMITH

2015. **Determination of cadmium by means of Reinecke salt.** O. A. Songina. *Uch. Zap. Kazakh. Univ.*, 1954, **16**, 58–64; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,442.—To the neutral solution (≃ 100 ml), in the absence of Pb, Cu, Ag, Hg and Tl, are added 2·5 ml of conc. H_2SO_4, 20 ml of 5 per cent. thiourea soln. and 15 ml of freshly prepared and filtered Reinecke salt soln. (concn. not stated) containing 1 per cent. of thiourea. With Cd >30 mg the amount of Reinecke salt is increased; an excess is not harmful. A pink ppt. of the Cd compound appears at once. The soln. is kept at 0° C with periodic shaking for 0·5 to 1 hr. The ppt. is filtered off on a sintered-glass filter, No. 3 or 4, washed first with 1 per cent. thiourea soln. and then with ethanol, and dried at 110° to 120° C. An empirical factor is determined for each batch of precipitant. The error with >10 mg of Cd is ≃ ± 1 per cent. Cadmium can be determined in the presence of considerable amounts of Zn.
G. S. SMITH

2016. **The titrimetric determination of cadmium with potassium ferrocyanide.** G. A. Segar (Applied Ion Exchange Dept., The Permutit Co. Ltd., Gunnersbury Avenue, London). *Analyst*, 1956, **81**, 65–66.—In the semi-micro method of Frost (*Analyst*, 1943, **68**, 51) for the determination of Zn, with buffering of the soln. with NH_4Cl - HCl and titration at the boiling point, the colour development of the indicator (*o*-dianisidine) was found to be not wholly satisfactory. Replacement of the buffer system by $(NH_4)_2SO_4$ - H_2SO_4 or by ammonium acetate - acetic acid greatly improves the clarity of the colour and the titration can then be made at room temp. Further improvement is effected by addition of the $K_3Fe(CN)_6$ just before the end-point is reached and before addition of the indicator in a duplicate titration. Efficient stirring is essential and use of a magnetic stirrer is recommended. The method is equally applicable to Cd and Zn. The end-point is reversible and over-titration can be corrected by addition of a standard soln. Copper, Fe and other substances forming ferrocyanide complexes, also reducing and oxidising agents, NO_2' and PO_4''' interfere, and Cl′ and NO_3' should be reduced to min. amounts. A. O. JONES

2017. **Method for determination of mercury in ores and smelting products.** F. Ensslin, H. Dreyer and O. Lessmann (Unterharzer Berg- und Hüttenwerke, Goslar, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 25–29.—For the determination of < 0·8 per cent. of Hg in sulphide ores (such as zinc blende), the Hg is freed from most other metals by distillation as $HgCl_2$ from HCl - H_2SO_4 solution and then determined by the dithizone method (*cf. Anal. Abstr.*, 1956, **3**, 945). Only traces of As, Sb, and Ge are carried over and these do not interfere. Good agreement is shown with values obtained gravimetrically by HgS pptn. J. P. STERN

2018. **The diethyldithiocarbamate of mercury: composition, structure and analytical application. A heterometric study.** M. Bobtelsky and R. Rafailoff (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (3), 247–252.—In the heterometric titration of Hg^{++} with Na diethyldithiocarbamate in acetic acid or acetate soln. at 20° C, the first max. extinction point is attained exactly at the end of the formation of insol. $Hg(CBM)_2$ (CBM = diethyldithiocarbamate ion), whatever excess of CBM is used. From 0·3 to 1·2 mg of Hg^{++} in 20 ml of aq. soln. containing, *e.g.*, 2 ml of 0·1 *M* acetic acid, can be titrated heterometrically with 0·004 *M* Na(CBM) soln., or conversely, 0·5 to 1 mg of Na(CBM) in 20 ml of aq. soln. can be titrated with 0·002 to 0·004 *M* aq. $Hg(NO_3)_2$, the error in each instance being negligible. Both titrations can be made in acid, alkaline or ammoniacal soln.

W. J. Baker

2019. **Analytical studies of boron. V. Ultramicro detection of boron on filter-paper.** Satoru Muto (Faculty of Tech., Gumma Univ., Tenjin-cho, Kiriu). *Japan Analyst*, 1955, **4** (9), 572–574.—The limit of detection (0·2 μg) of B with curcumin is lowered to 0·02 μg (limit of concn., 1 in 10^6) by restricting the diffusion of the sample spot on the paper with a ring of paraffin wax. The paper is impregnated with a 0·1 per cent. ethanolic soln. of curcumin and a ring (inner diameter 5 mm, outer diameter 9 mm) is stamped on it with paraffin wax (m.p. 60° C). An acidic soln. of the sample (> 0·01 ml) is spotted and dried at > 60° C. The paraffin wax melts and prohibits further diffusion of the sample soln. When an organic acid such as oxalic, salicylic or tartaric is added to the sample soln., the limit of detection is lowered still further (*e.g.*, in the presence of oxalic acid, to 0·002 μg of B).

K. Saito

2020. **Colorimetric determination of aluminium by means of the reagent "arsenazo."** V. I. Kuznetsov and R. B. Golubtsova. *Zavod. Lab.*, 1955, **21** (12), 1422–1426.—At pH 4·3, "arsenazo" (*cf. Anal. Abstr.*, 1956, **3**, 1263) gives a violet coloration with Al (Kuznetsov, *Dokl. Acad. Sci. USSR*, 1954, **50**, 227). Colours are also given with ZrO_3^{--}, Hf, Ga, In, Pd, Fe^{+++}, Th and Ti; Fe^{++}, Mg, Mn, alkaline-earth metals and alkali metals do not interfere. To determine ⩾ 5 μg of Al, 2 to 3 ml of the solution with an acidity ⩾ 0·02 to 0·03 *N* in HCl are mixed in a colorimeter tube with one drop of conc. HCl and 1 ml of water, then treated with 0·30 ml of 0·005 per cent. aq. arsenazo solution, followed by one drop of 10 per cent. ascorbic acid solution (to prevent interference from Fe^{+++}) and eight drops of 25 per cent. aq. hexamine solution to act as a buffer, mixing after each addition. It is essential to add the buffer solution after the reagent. The solution is diluted to 5·0 ml and the colour is compared with that of a scale of standards containing 0·0, 0·50, 0·65, 0·85, 1·10, 1·40, 1·85, 2·4, 3·1, 4·1 and 5·3 μg of Al, prepared by the use of a solution of Al in HCl treated as described above. Alternatively, by reason of the rapid development of colour, Al can be determined by colorimetric titration. A standard solution of Al containing 5 μg per ml is added to a solution containing the reagents until the colour matches that of the treated sample solution.

G. S. Smith

2021. **Determination of aluminium in alloy steels (cryolite method).** R. Leo and G. König (Inst. Foundry Technol., Leipzig, Germany). *Metallurgie u. Giessereitech.*, 1955, **5** (3), 26–28.—The determination of Al in alloy steel containing metals such as Mn, Cr, Co, Ni, W and Mo, described by Tananaev and Yakovlev (*Zavod. Lab.*, 1950, **16**, 1155), has been re-examined and the following procedure is recommended for samples with an aluminium content of ⩽ 0·5 per cent. Dissolve 0·5 to 1 g of the sample in aqua regia and fume the soln. with H_2SO_4. After cooling and filtering off the residue (SiO_2, carbon, H_2WO_4, etc.), reduce the Fe^{III} with zinc amalgam. Again filter and make weakly ammoniacal. For complexing purposes add ammonium oxalate and citrate, adjust the pH to 4·5 and precipitate Al by the addition of NaF. Filter off the ppt., wash and redissolve in H_3BO_3 soln. and a little HCl, and precipitate the Al with an acetic acid soln. of 8-hydroxyquinoline. Filter off the aluminium compound, and wash and weigh the ppt. as Al_2O_3. If the aluminium content of the alloy is < 0·5 per cent., take a 5-g sample, dissolve it in HCl, oxidise the Fe and extract with ether. After fuming with H_2SO_4 carry out the above procedure.

Chem. Abstr.

2022. **Simple spot-tests for aluminium contaminants.** H. S. Hilborn and R. C. Pugh (E. I. du Pont de Nemours & Co., Augusta, Georgia, U.S.A.). *Nucleonics*, 1955, **13** (10), 46–47.—Contamination or inclusions by Fe, Pb, Mg, Hg, Mo, Ni, Sn, Cu or U on the surface of aluminium metal are detected by electrolysis into a filter-paper pad moistened with an appropriate electrolyte (acetic acid, HNO_3, KNO_3 or K_2SO_4) and held between the sample (anode) and a stainless-steel or aluminium cathode. A potential of 6 V is applied for 30 to 60 sec. The pad is finally spotted with a reagent specific for each metal ion in turn.

E. N. Jenkins

2023. **Volume - gravimetric method of determining the thickness of oxide films on electropolished aluminium.** P. V. Shchigolev (Inst. Phys. Chem., Acad. Sci., U.S.S.R.). *Zavod. Lab.*, 1955, **21** (12), 1474–1476.—The method is based on the fact that oxide and other non-metallic films dissolve in 0·3 to 0·5 *N* NaOH without liberating H, and a measurement of the vol. of H evolved can be related to the amount of metal dissolved. With samples of equal area, attack in the solution is allowed to proceed until similar vol. of H are obtained. With samples of different areas, similar vol. per unit area are used. The samples are weighed before and after treatment with NaOH. Electropolished and mechanically polished samples are compared. The difference between the loss in wt. in the two cases equals the wt. of the oxide film.

G. S. Smith

2024. **Separation of aluminium and gallium.** H. Specker and E. Bankmann (Inst. f. Spektrochem., Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 97–100.—Quantitative separation of $Ga(SCN)_3$ from $Al(SCN)_3$ can be carried out by one extraction of the aq. solution (4 *N* with respect to H_2SO_4) with an equal vol. of ether - tetrahydrofuran (2:3 by vol.). The method is effective for 20 mg of Al plus Ga in 50 ml of aq. phase and ratios of Al to Ga of 1:1 to 1000:1.

J. P. Stern

2025. **The spectrochemical determination of indium in cassiterite.** D. F. C. Morris and F. M. Brewer (Oxford Univ., England). *Anal. Chim. Acta*, 1956, **14** (2), 183–185.—The cathode-layer carbon arc is used with a large Hilger Littrow quartz spectrograph. The spectral lines selected are the 3039·4-A line of In and the 3032·8-A line of Sn, used

as internal standard. The method is suitable for the determination of concn. of In > 0·001 per cent. and the precision is within ≃ 5 per cent.
W. C. JOHNSON

2026. **Amperometric determination of thallium by the anodic bromide method.** O. A. Songina and A. P. Voĭloshnikova (State Univ., Kazakh. SSR). *Zavod. Lab.*, 1956, **22** (1), 19–24.—Conditions for the reduction of $Tl^{\cdot\cdot\cdot}$ on a rotating platinum microelectrode in H_2SO_4, acetic acid, and KNO_3, and the anodic oxidation of Br' in H_2SO_4 solutions of various concn. are studied. The Br - Br′ system is reversible on the platinum electrode. The use of the diffusion current of oxidation of Br' is recommended for the amperometric determination of Tl. Thallous ions are oxidised to $Tl^{\cdot\cdot\cdot}$ by means of permanganate or persulphate and the excess of oxidant is removed. The acidity for the amperometric titration can vary within wide limits, but 2 *N* H_2SO_4 as a medium is recommended. Titration is carried out with 0·001*M* KBr for < 0·1 mg of Tl in 20 ml of solution, with 0·01 *M* for 0·1 to 1 mg of Tl, and with 0·1 *M* for > 1 mg of Tl in 20 ml. The potential used is +1·3 V *vs.* the mercury iodide electrode.
G. S. SMITH

2027. **Separation of rare earths from thorium nitrate.** M. W. Lerner and G. J. Petretic (U.S. Atomic Energy Commission, New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 227–229.—In the separation described, most of the Th can be extracted with a pre-equilibrated mixture of "penta-ether" (tetraethylene glycol dibutyl ether), diethyl ether and 8 *M* HNO_3, followed by removal of the residual Th and Fe, Ti, etc., with an oxine - $CHCl_3$ mixture. The rare earths (Dy, Gd, Sm, Eu and Er) are then pptd. as oxinates, with La as carrier. The separation takes ≃4 hr. and the recovery of each rare-earth element is from 90 to 96 per cent. The addition of diethyl ether accelerates the phase separation in the 8 *M* HNO_3 - penta-ether system. A sample of ≃ 50 g of $Th(NO_3)_4.4H_2O$ is preferred (10 to 25 g for crude samples); the concn. of oxine should be 20 per cent. w/v, extraction being made at pH 4·2. The method is applicable to the spectrographic determination of rare earths.
W. J. BAKER

2028. **The chemical analysis of the rare-earth elements. X. Separation of praseodymium by electrolytic oxidation in fused hydroxide melts.** Seozo Misumi (Yamagata Univ., Koshirakawa-cho, Yamagata). *Japan Analyst*, 1955, **4** (9), 549–552.—When a mixture (< 100 mg) of $Nd(OH)_3$ and $Pr(OH)_3$ is electrolytically oxidised in a melt in KOH (15 g) at 260° to 300° C for 30 min. (3·5 to 3·8 V; 0·5 amp.; anode, nickel crucible; cathode, platinum wire), an insol. higher oxide of Pr (empirical formula $PrO_{1\cdot83}$) is produced. When the product is leached with water, a mixture of the higher oxide of Pr and $Nd(OH)_3$ remains undissolved. The $Nd(OH)_3$ is extracted with 0·1 per cent. acetic acid (10 to 40 ml) together with a small amount of Pr which has not oxidised, whilst the higher oxide of Pr remains unchanged. Traces of Ni are removed with aq. NH_3 soln. (1 + 1, 10 to 20 ml). The purity of the higher oxide is ≃ 95 per cent. By repeating the same procedure two or three times the purity is increased to 98 per cent., but not more.
K. SAITO

2029. **A new eluent for the separation of the actinide elements.** G. R. Choppin, B. G. Harvey and S. G. Thompson (Radiation Lab., Univ. Calif. Berkeley, Calif., U.S.A.). *J. Inorg. and Nuclear Chem.*, 1956, **2** (1), 66–68.—Ammonium α-hydroxybutyrate soln. (0·4 *M*) is more efficient than ammonium lactate in separating individual rare-earths or actinide elements by successive elution at pH 3·8 to 4·8 and 87° C from a 5-cm × 2-mm column of Dowex-50 X-12 cation resin.
E. N. JENKINS

2030. **The analysis of cyanogen compounds. III. Volumetric determination of cyanate.** Shinsuke Takei (Faculty of Eng., Tohoku Univ., Sakurakoji, Sendai). *Japan Analyst*, 1955, **4** (8), 479–481.—Cyanate ions (≃ 0·1 *M*) are pptd. with 4 *M* pyridine (5 to 7 ml) and *M* $CuSO_4$ (2·5 ml) from an acetic acid soln. and extracted with chloroform (4 × 5 ml). The chloroform layer is washed with 2 per cent. pyridine soln. containing 0·2 per cent. of $CuSO_4.5H_2O$ and the complex is decomposed with 6 *N* HCl. The aq. layer is neutralised with Na_2CO_3 soln., then made acid with glacial acetic acid (2 ml) and treated with KI (2 g) to produce iodine, equiv. in amount to the cyanate, which is titrated with $Na_2S_2O_3$ soln. by the usual method. The presence of cyanide vitiates the estimation. Neither NH_4^+ (< 600 mg) nor Cl' (< 100 mg) interfere.
K. SAITO

2031. **Determination of silicon in titanium and titanium alloys.** K. Jordan and R. W. Fischer. *Tech. Mitt. Krupp*, 1955, **13** (2), 39–43.—A photometric method was developed, for analyses in industrial operations, which is very fast, very sensitive and permits the determination of 0·005 to 0·1 per cent. of Si within ± 0·002 per cent. and of 0·1 to 1 per cent. within ±0·02 per cent. *Procedure*—Dissolve the sample in HF and add boric acid, which binds excess of HF, oxidise the Ti with $KMnO_4$ soln. and precipitate by boiling; the excess of $KMnO_4$ is decomposed. To the filtered soln. add ammonium molybdate to form yellow molybdosilicic acid. After some time the Si-containing compound is reduced by $NaHSO_3$ and tartaric acid to form a blue compound, which can be measured photometrically.
CHEM. ABSTR.

2032. **Activation analysis of trace impurities in germanium using scintillation spectrometry.** G. H. Morrison and J. F. Cosgrove (Sylvania Electric Products Inc., Flushing, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 320–323.—A method based on the use of neutron activation analysis is described for the quant. determination of trace impurities in Ge. Only those elements resulting in radionuclides with half-life > ≃ 4 hr. and < 200 days can be determined easily. Gamma-scintillation spectrometry is used to identify and measure the amounts of the various impurities after chemical separation. A sensitivity of 0·001 to 1 μg is attainable for most elements. The precision has a standard deviation of about ± 3 per cent. and the accuracy a standard deviation of as much as ± 30 per cent. in some cases, owing to chemical loss during the separation procedure.
K. A. PROCTOR

2033. **Colorimetric determination of traces of tin with dithiol.** Hiroshi Onishi and E. B. Sandell (Univ. Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (2), 153–161.—The method described is suitable for the photometric determination of 3 to 50 μg of Sn with an error of

< 20 per cent. for > 20 μg. The visual method is suitable for amounts of Sn < 3 μg, with an accuracy of ± 0·5 per cent. Any As, Sb or Ge present in the sample soln. is first removed by distilling from H_2SO_4 in the presence of hydrazine sulphate and KH_2PO_4 at a temp. of 155° to 165° C while passing CO_2 and adding 6 *N* HCl dropwise. The Sn is then distilled in a similar manner at 145° to 160° C while adding a mixture of 6 *N* HCl and aq. HBr (48 per cent.). The distillate is heated with H_2SO_4 and HNO_3, evaporated to fuming, and the residue is diluted to 7 ml with water. To this soln. are added 1 drop of thioglycollic acid, 0·05 ml of Santomerse S (dispersing agent) soln. (1 + 19) and 0·5 ml of a 0·2 per cent. soln. of dithiol in 1 per cent. NaOH soln. After heating at 50° ± 5° C for 5 ± 1 min., 0·5 ml of Santomerse S soln. (1 + 3) is added, the soln. is cooled, diluted to 10 ml, and its absorption at 530 mμ is measured at once. A calibration curve is prepared similarly. For the visual determination of < 3 μg of Sn, the method is modified to produce a smaller final volume and the dispersing agent is omitted. Directions are given for the preliminary treatment of silicate rocks, iron and sulphides. Selenium, if present, must be removed from the distillate by reduction with SO_2 and filtration. The procedure has been used to determine Sn in various mixtures containing As, Bi, Fe, Mo, Sb, W, Hg, Se, Te, Ru, Os and Re.

W. C. JOHNSON

2034. **Determination of small amounts of tin in ores.** I. A. Blyum and N. G. Zȳryanova (Lab. of the "Uraltsvetmetrazvedka" Trust). *Zavod. Lab.*, 1956, **22** (1), 46–47.—To determine ≃ 0·005 to 0·1 per cent. of Sn in ores of any kind, 1 to 2 g of the ore, first heated to between 500° and 550° C if a sulphide ore, are fused in an iron crucible with 5 to 10 g of Na_2O_2, and the melt is extracted with water. The solution is diluted to a vol. of 200 to 250 ml, and treated first with HCl to dissolve hydroxides, then with aq. NH_3. The ppt. is filtered off and dissolved in 40 to 50 ml of a mixture (4:1) of dil. H_2SO_4 (1 + 1) and conc. HCl or, for germanium ores, in 50 to 60 ml of dil. HCl (3 + 1) followed by boiling with 1 to 2 ml of H_3PO_4 for 30 to 40 min. to reduce the vol. to 15 to 20 ml, and then mixing with 40 to 50 ml of dil. H_2SO_4 (1 + 1). The solution is treated with 10 ml of HBr and distilled in a stream of CO_2. When the temp. reaches 180° C, 15 to 20 ml of HBr are introduced dropwise at 2 to 3-sec. intervals from a dropping-funnel. The final temp. is 215° to 220° C. The distillate (150 to 200 ml) is mixed with 50 mg of $FeCl_3$ or $Fe_2(SO_4)_3$ and pptd. at 70° to 80° C with aq. NH_3. The ppt. is filtered off, washed with 2 per cent. NH_4Cl solution, and dissolved in hot dil. HCl (1 + 1), and the solution is made up to 20 ml with dil. HCl (1 + 1). To 15 ml of the solution is added 0·2 g of iron powder reduced in H and, after 15 min., 10 ml are filtered and the tin content is determined polarographically after addition of four drops of 0·5 per cent. gelatin solution and passage of H for 2 to 3 min.

G. S. SMITH

2035. **The analysis of solder-type alloys by density.** J. Davis, A. J. Easton and J. Freezer (Ever Ready Battery Ltd., London). *Sheet Metal Ind.*, 1955, **32** (335), 208–210.—The chemical composition of solders used in the electrical industry can be controlled to within ± 0·5 per cent. of Sn by measuring the density of the sample (≮ 4 g) at 20° C, a small flask of air-free dist. H_2O being used and removing air-bubbles from the surface of the alloy. Composition *vs.* density curves are given for drawn solder-wire (20 to 60 per cent. of Sn), "blow-pipe solder" (38·5 to 41 per cent. of Sn) and cored solder (18·5 to 21 per cent. of Sn). The absence of a resin-flux core from parts of the same reel can thus be detected. The method is also applicable to Zn - Pb - Cd alloys of const. cadmium content, the density varying by 0·02 g per cu. cm for lead contents of 0·9 to 1·0 per cent.; the accuracy is within ± 0·03 per cent. of Pb.

W. J. BAKER

2036. **Use of pyrazolone derivatives in analytical chemistry. Qualitative and quantitative determination of titanium by means of diantipyrinyl-o-hydroxyphenylmethane.** S. I. Gusev and R. G. Belles. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 68–76; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,450.—Diantipyrinyl-*o*-hydroxyphenylmethane (**I**) gives yellow colours with Ti^{III} and Ti^{IV} in acid medium. The colour intensity with Ti^{III} over the concn. range 2 to 30 μg of Ti per ml follows Beer's law. The min. amount detectable is 0·35 μg per ml. Interference is caused by W^{VI} and Mo^{VI}. The brown colour given by Fe^{III} disappears on addition of H_3PO_4; Fe^{II} does not give a colour. A ppt. sol. in ethanol is given by V^{V}, but reduced soln. do not react. Salts of Bi, Sn and Sb give white ppt. sol. in aq. ethanol. Lead salts give white cryst. ppt. which do not interfere with the detection of Ti. Uranyl ions give a green - yellow colour which disappears on acidification. To detect Ti in the presence of Fe^{III}, the solution (vol. not stated) is mixed with the reagent soln. (100 ml of 2 per cent. **I** as hydrochloride in 96 per cent. ethanol, 10 drops of conc. H_2SO_4 and 0·1 to 0·2 g of quinol) and, after 30 min., with a few drops of conc. H_3PO_4. The soln. becomes colourless if Ti is absent and yellow if Ti is present. To detect Ti in the presence of Fe^{III}, V^{V} and Cr^{VI}, the solution is acidified with HCl and reduced with Zn until a negative reaction for Fe^{III} is given by SCN^{-}. The reagent is then added. To determine Ti in steel, the sample containing ≃ 1 mg of Ti is dissolved in the usual way, the solution is diluted to 100 ml and a 5-ml aliquot is mixed with 4·5 ml of reagent soln. After 30 min., 10 drops of H_3PO_4 are added and the colour intensity is measured against standards. The colour is stable and is not affected by HNO_3. Higher concn. (> 10 per cent.) of HCl hinder the colour development. Sulphuric acid is harmful and at concn. > 5 per cent. completely prevents the development of colour. The synthesis of the reagent from phenazone and salicylaldehyde is described. The complex with Ti^{III} is formulated as $C_{29}H_{27}O_3N_4Cl_2Ti$.

G. S. SMITH

2037. **Phase analysis of titanium-base alloys.** N. I. Blok, A. I. Glazova and N. F. Lashko. *Zavod. Lab.*, 1956, **22** (1), 35–38.—Electrolytic phase separation of titanium alloys is carried out in a solution containing 2 g of KSCN and 10 g of citric acid in 1200 ml of methanol, initially at − 7° to − 10°C and not allowed to rise above 0° C. These conditions suppress the hydrolysis of titanium salts. Other conditions are—a membrane of cellulose acetate, current density 0·013 amp. per sq. cm, voltage 30 V for 1 to 2 hr., the anode is the sample in cylindrical form (40 mm high and 13 mm in diameter), and the cathode is a rustless-steel sheet. The anode ppt. is separated and subjected to X-ray analysis. The method permits the β-phase and

TiC to be separated from Ti - Cr and Ti - Cr - C alloys, and the α-phase, $TiCr_2$ and TiC from Ti - Cr - Al - C alloys. G. S. SMITH

2038. **Azo dyestuffs as organic reagents. I. Detection of zirconium with 4-(*p*-dimethylaminophenylazo)diphenylarsinic acid.** Kiyo Tsuji, Mayumi Kageyama, Setsuko Nakamura and Takeo Ueda (Japan Women's Univ., Takata-toyokawa-cho, Bunkyo-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (11), 1180–1184.—The reactions between Zr and diphenylarsinic acid and its derivatives were studied with reference to their use for the detection of Zr. 4-(*p*-Dimethylaminophenylazo)diphenylarsinic acid (**I**) and 4:4′-bis(*p*-dimethylaminophenylazo)-diphenylarsinic acid (**II**) were synthesised by coupling dimethylaniline with diazotised *p*-amino-diphenylarsinic acid (obtained by the catalytic reduction of *p*-nitrodiphenylarsinic acid) and diazotised *pp*′-diaminodiphenylarsinic acid (obtained from *p*-nitrophenyldichloro-arsine), respectively. Filter-paper impregnated with a 0·1 per cent. soln. of **I** and **II** in ethanol is used for the spot test for Zr (> 0·1 μg, in 0·05 ml). In the presence of Zr, the spot turns brown when treated with 0·2 *N* HCl at 50° to 60° C. The compositions of the brown ppt. are $Zr(\mathbf{I})_4.HCl$ and $Zr(\mathbf{II})_4.2HCl$. The interference of WO_4'', MoO_4'', $Ti^{\cdots\cdot}$ and $Ce^{\cdots\cdot}$ can be eliminated without affecting the sensitivity by the use of H_2O_2. Both reagents are an improvement on the conventional *p*-dimethylaminoazophenylarsonic acid. K. SAITO

2039. **Ultra-violet spectrophotometric determination of zirconium.** R. B. Hahn and L. Weber (Wayne Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 414–415.—A spectrophotometric method for the determination of milligram amounts of Zr in the presence of 100 mg of Al, 10 mg of Fe and 20 mg of Ti is described. Errors occur when larger quantities of these ions are present and the accuracy is poor in samples containing < 1 mg of Zr. The Zr is precipitated as the tetramandelate, which dissolves in aq. NH_3 to form a soluble, salt-like compound which exhibits max. absorption at 258 mμ. Excess of mandelic acid is removed by alcohol and ether washings. The amount of aq. NH_3 used is not critical and the solutions are stable for two days. K. A. PROCTOR

2040. **Titrimetric determination of zirconium in magnesium alloys.** P. J. Elving and E. C. Olson (Univ. of Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 251–252.—The rapid and accurate procedure described for the determination of 0·4 to 0·8 per cent. of Zr in magnesium alloys is based on acid dissolution of the sample (2 to 3 g) according to Papucci's method (*Anal. Abstr.*, 1955, **2**, 3017), followed by direct amperometric titration of Zr in each of the two soln. (acid-sol. and acid-insol. Zr) with 0·01 to 0·02 *M* cupferron in 10 per cent. H_2SO_4. The current is read 1 to 1·5 min. after each addition at a potential between − 0·84 and − 1·0 V *vs.* the S.C.E.; the equivalence-point vol. is obtained from the titration curve. By dissolution (0·5 g sample) in 10 ml of 10 per cent. H_2SO_4, followed by evaporation to fumes of SO_3 with conc. H_2SO_4 (5 ml), all the Zr can be brought into soln. and the titration made after dilution to 50 ml. No interference is caused by F′, PO_4''' and SO_4''; $Fe^{\cdots}$ tend to concentrate in the acid-insol. fraction. W. J. BAKER

2041. **The colorimetric determination of thorium using 1-(2-arsonophenylazo)-2-naphthol-3:6-disulphonic acid.** J. Clinch (Thorium Ltd., Ilford, Essex, England). *Anal. Chim. Acta*, 1956, **14** (2), 162–171.—The reaction between $Th^{\cdots\cdot}$ and 1-(2-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (APANS) has been investigated. The red colour produced is stable in the cold, unstable above 35° C and is intensified by a temp. rise in the range 15° to 25° C. The colour intensity is reproducible only in the pH range 0·5 to 1·5. For the colorimetric determination of Th the following conditions are applied. *Procedure*—To the soln., containing up to 1·3 mg of $Th^{\cdots\cdot}$, add 2 drops of 1 per cent. phenolphthalein soln. and dil. aq. NH_3 (1 + 1) to produce a red colour. Add 10 ml of dil. HCl (1 + 4), 5 ml of aq. hydroxylamine hydrochloride (1 + 10) and 15 ml of 0·1 per cent. aq. APANS soln., and dilute to 100 ml. Immerse in a thermostat at 25° C for 15 min., then measure the optical density in a 1-cm cell on a Hilger Spekker absorptiometer with a mercury vapour lamp and Wratten 77, Ilford 605 and Calorex filters. As a comparison soln. use a blank containing the reagents only. Prepare a calibration curve by the same procedure. No Sn^{II}, Sn^{IV}, Ti^{IV} or Zr^{IV} must be present. The following interfere and are represented in decreasing order of effect—F′, Fe^{III}, PO_4''', $UO_2^{\cdot\cdot}$, SO_4'', Ce^{III}, Fe^{II}, Li, Pb, Al, Ca, Ba, K, NO_3', Na, $NH_4^{\cdot}$. The effect of F′ can be minimised by adding 10 mg of $Al^{\cdots}$ as chloride or nitrate. Interference from 5 mg of lanthanons can be neglected. To determine Th in monazite, it is first pptd. as oxalate, the oxalate is destroyed with conc. $HClO_4$ and conc. HNO_3 and the above procedure is applied. W. C. JOHNSON

2042. **Diphenic acid as an analytical reagent. III. Separation of thorium from different elements and monazite sands.** G. Banerjee (Gov. Coll., Darjeeling, India). *Z. anal. Chem.*, 1955, **148** (2), 105–110.—Diphenic acid will precipitate Th quant. from soln. containing cerite earths provided that the ratio of ThO_2 to cerite earth is ≮ 1:26; if a double-pptn. technique is employed, then the ratio can be 1:44. *Procedure*—The soln. of Th and cerite earths is nearly neutralised to Congo red, and ≃ 0·2 g of ammonium acetate is added. A 0·1 *M* soln. of diphenic acid is added, with stirring, to the boiling sample soln., which is boiled for a further 2 min. After 5 min., the ppt. is filtered off on a fine-porosity sintered crucible, and is washed successively with 0·01 *M* diphenic acid soln., hot H_2O and hot ethanol, before being dried for 2 hr. at 110° to 115° C. The ppt. has the formula $Th(C_{14}H_8O_4)_2$. The metals Al, Zn, Mn, Ca, Sr, Ba, Cu, Cd, Pb, Sn, Bi, Mg and Pd, and the anions PO_4''', AsO_4''' and MoO_4'' do not interfere, neither do Cr, Ni and Co if double pptn. is employed. If the metals Ag and Hg (as $Hg_2^{\cdot\cdot}$) are present, they are masked by the addition of 1 g of thiourea. Zirconium and Fe are co-pptd. with Th, and their separation has been described earlier (*Anal. Abstr.*, 1956, **3**, 1307). Thorium can be separated from U if the ratio of ThO_2 to U_3O_8 is ≮ 1:25, or, with a double pptn., ≮ 1:80. By using diphenic acid, Th can be separated from monazite-sand extracts in a single pptn. J. H. WATON

2043. **Theoretical basis of the thymol - hypobromite reaction for ammonia.** L. N. Lapin. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 77–85; *Ref. Zhur., Khim.*, 1955, Abstr.

No. 26,479.—The reaction for ammonia based on the development of an intense blue colour on the addition to soln. of ammonium salts of phenol and hypobromite takes place in three stages. The first, most specific and characteristic, phase is the formation of *p*-aminophenol; the second is the conversion of *p*-aminophenol into a halogen derivative of quinoneimine; and the third is the synthesis of indophenol. With thymol in place of phenol the indophenol formed passes into the organic solvent and widens the range of application of the reaction. Detection is not masked by the formation of a ppt. Most organic and inorganic compounds, except certain primary amines, do not interfere. *Procedure*—To 5 ml of the soln. to be tested in a large test-tube is added 1 ml of 25 per cent. thymol in ether, the mixture is shaken and 12 to 15 ml of hypobromite (1 vol. of 2 *N* NaOH and 2 vol. of saturated bromine water) are added in small portions. After several min., 5 ml of ether or 3 ml of xylene are added and the colour is transferred to the organic solvent. By means of this method 0·01 mg of NH_3 can be detected in 100 ml of soln. Ammonia in biological material can be detected without preliminary treatment.

G. S. SMITH

2044. **Spectrophotometric determination of small concentrations of hydrazine in water.** R. Freier and G. Resch (Volkswagenwerk, Wolfsburg, Germany). *Z. anal. Chem.*, 1956, **149** (3), 177–181.—The method of Watt and Chrisp (*Brit. Abstr. C*, 1953, 161) is used (H_2SO_4 instead of HCl being adopted for acidification) and its scope is extended to the determination of 5 to 5000 μg of hydrazine per litre. *Procedure*—Treat the aq. sample (10 ml) with 2 per cent. alcoholic *p*-dimethylaminobenzaldehyde (10 ml) and conc. H_2SO_4 (1 ml), cool to between 20° and 25° C and dilute to 50 ml. Determine the extinction at 458 mμ after 10 min. J. P. STERN

2045. **Applications of nitrometry. IV. Determination of nitrous acid.** Masaharu Yamagishi and Makoto Yokoo (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (9), 957–958.—It was found that ammonium sulphamate (**I**) reacts with nitrous acid in an acetic acid soln. to yield an equiv. amount of gaseous N, which can be volumetrically determined (on a micro scale) in a nitrometer. The sample soln. (KNO_2, 40 to 350 μg in 1 ml) is introduced with water (7 ml) into a nitrometer confined with saturated NaCl soln. Carbon dioxide is passed through to expel O from the nitrometer, which is then partly evacuated. An acidic soln. of **I** (1 g in 25 ml containing 5 ml of glacial acetic acid, saturated with $NaNO_3$) (0·5 ml) is introduced and the whole is shaken for 2 min. Sodium hydroxide soln. (40 per cent.) (1 ml) is introduced into the nitrometer to absorb all the CO_2. The volume of the remaining gas, which comprises pure N, is measured and the amount of nitrite is calculated. The result is in good agreement with those by the $KMnO_4$ titration method.

K. SAITO

2046. **Use of a cationite in the analysis of phosphorites.** Sh. T. Talipov and T. I. Fedorova. *Trudy Sredneaziat. Gosudarst. Univ.* (*Tashkent*), *Khim. Nauk.*, 1954, **55** (7), 135–140; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,501.—A rapid method of determining P_2O_5 and the sesquioxides in phosphorites by means of Wofatit in the H form is described. The sample (0·5 to 1 g) is dissolved in 15 to 25 ml of conc. HCl, the solution is boiled gently for 30 min. and heated over boiling water for 40 to 45 min. after becoming dry. The residue is moistened with 2 to 4 ml of HCl (1 + 1) and dissolved in hot water, the insoluble matter is filtered off and washed with water, and the filtrate is made up to 100 ml. The solution is passed through a column of Wofatit during 10 to 15 min., the column is washed until the washings are neutral to methyl orange, and the filtrate is made up to 300 or 500 ml in a calibrated flask. To determine PO_4''', 100 ml of the soln. are titrated with 6 *N* NaOH, in the presence of methyl orange - indigo carmine mixed indicator, until the soln. is green, 5 drops of 1 per cent. alcoholic methylene blue soln. are added, and the soln. is titrated with 0·1 *N* NaOH to a pure green colour. Phenolphthalein (20 drops of 1 per cent. soln.) is added and the soln. is titrated with 0·1 *N* NaOH to a grey end-point corresponding to the second equivalence point. The result is calculated to P_2O_5. The cations adsorbed by the column are extracted with 50 to 70 ml of conc. HCl, the column is washed with dil. HCl and water, and aq. NH_3 soln. is added to the filtrate to ppt. the sesquioxides, which are then ignited. The relative errors are $\pm$ 2·7 per cent. for P_2O_5 and $\pm$ 1·2 per cent. for P_2O_3. The method is applicable to raw materials and products of superphosphate works. G. S. SMITH

2047. **Analysis of mixtures of the condensed phosphates by ion-exchange chromatography. II. Mixtures of ortho-, pyro-, tri-, tetra-, trimeta-, and tetrameta-phosphates and Graham's salt.** T. V. Peters, jun., and W. Rieman III (Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (2), 131–135.—Condensed phosphates are separated on a column of Dowex 1-X8 resin that has been specially purified and graded to 100 to 200 mesh. Elution with KCl soln. buffered at pH 5·0 yields (1) orthophosphate, (2) pyrophosphate, (3) triphosphate, (4) a mixture of tetra- and tetrameta-phosphates, and (5) trimetaphosphate in separate fractions. Elution with KCl soln. buffered at pH 9·0 yields (*i*) a mixture of ortho-, pyro-, tri- and tetra-phosphates, (*ii*) tetrametaphosphate, and (*iii*) trimetaphosphate. In both elutions Graham's salt is retained on the column until it is treated with 3 *M* HCl. Thus two elutions serve for determination of the seven constituents.

W. C. JOHNSON

2048. **Analytical chemistry of phosphates. II. A new volumetric determination of pyrophosphate in the presence of ortho- and meta-phosphates.** Takio Kato, Zenzi Hagiwara and Ryojiro Shinozawa (Tohoku Univ., Sakurakoji, Sendai). *Japan Analyst*, 1955, **4** (8), 486–490.—The method of determination of pyrophosphate reported in Part I (*cf. Anal. Abstr.*, 1955, **2**, 2697) can be applied, with slight modifications, to the determination in the presence of ortho- or trimeta-phosphate. Pyrophosphate is pptd. with Zn acetate at pH 3·8 to 3·9; the ppt. is filtered off, washed with water, dissolved in 2 *N* aq. NH_3 soln. and titrated with standard EDTA (disodium salt) soln., with Eriochrome black T as indicator. K. SAITO

2049. **Analytical chemistry of quinquevalent phosphorus. III. Determination of the phosphorus pentoxide content of metal orthophosphate solutions.** J. Fischer and G. Kraft (Inorg. Chem. Inst., Goethe Univ., Frankfurt am Main, Germany). *Z.*

anal. Chem., 1956, **149** (1–2), 29–40.—The total phosphorus pentoxide content (second equivalence point) of metal phosphate solutions is determined by titration with NaOH. During titration, interference occurs owing to pptn. of neutral or basic salts, which then lose H^+ to the supernatant solution. Addition of K oxalate as a complexing reagent obviates interference by Zn, Mn, Cu, Ni, Co, Cd, Fe^{II}, Al and alkaline-earth metals (though Fe^{III} still interferes) and permits the second equivalence point to be determined potentiometrically to within $\pm$ 0·5 per cent. By the use of dimethyl yellow and of phenolphthalein as colour indicators, accuracies within $\pm$ 3 per cent. may be attained. The metal content of the solution can be deduced from the H^+ liberation of the uncomplexed ppt. with an accuracy within about $\pm$ 10 per cent.

J. P. STERN

2050. **Study of the colorimetric determination of phosphorus and arsenic in steel.** M. Jean. *Anal. Chim. Acta*, 1956, **14** (2), 172–182.—The proposed methods depend on the formation of molybdophosphoric and molybdoarsenic acids and their reduction to produce a blue coloration. The two acids are separated by extracting the former from aq. solution with a mixture of ether and amyl alcohol. The conditions governing the formation, separation and reduction of the acids have been investigated in detail, and it is found that the addition of $Bi^{\cdots}$ enables the reduction to take place in the cold. The methods have been used for the determination of P and As in steels containing S, Mn, Si, Cu and Cr.

W. C. JOHNSON

2051. **Reagent for the colorimetric determination of phosphate and arsenate.** F. L. Hahn and R. Luckhaus (Lab. Control Quím., Durango 283, Mexico 7). *Z. anal. Chem.*, 1956, **149** (3), 172–177.—Zindzadze's (*Ibid.*, 1930, **82**, 383) molybdenum-blue reagent for the determination of $PO_4^{\prime\prime\prime}$ and $AsO_4^{\prime\prime\prime}$ is very inconvenient. To obtain an equally effective reagent less laboriously, dissolve 6·58 g of $Na_2MoO_4.2H_2O$ and 400 mg of hydrazine sulphate in 100 ml of water and add 100 ml of conc. H_2SO_4. Cool the deep-blue solution, dilute with 500 ml of water, and after further cooling make up to 1 litre. This pale-brown stock solution is used as required. To determine $PO_4^{\prime\prime\prime}$, mix the sample solution (0·15 to 7·5 μg of P_2O_5 per ml) with one quarter of its vol. of reagent, cool, make up to the requisite vol., and determine the extinction at 640 mμ. For >2 μg per ml, the accuracy is well within $\pm$1 per cent.

J. P. STERN

2052. **Notes on the colorimetric determination of arsenic after volatilisation as arsine.** H. W. Berkhout (State Agric. Test and Res. Sta., Maastricht, Holland). *Chemist Analyst*, 1956, **45** (1), 24.—Certain modifications are recommended in the procedure for collecting As on cellulose powder impregnated with $HgBr_2$ and subsequent colorimetric analysis (Berkhout and Jongen, *Anal. Abstr.*, 1954, **1**, 2962). With the concn. of hydrazine stated, the molybdenum blue has a yellowish tinge, not obtained when 0·2 ml of 1 per cent. hydrazine soln. is used. With too much cellulose powder, some pptn. of Hg_2Br_2 may occur on reduction, and this is prevented by washing any unchanged $HgBr_2$ out with methanol.

E. J. H. BIRCH

2053. **The elimination of interference by arsenic in the polarographic determination of antimony and tin.** G. Packman and G. F. Reynolds (Chem. Inspectorate, Min. Supply, Kidbrooke, London). *Analyst*, 1956, **81**, 49–52.—The erroneous results sometimes obtained in the polarographic determination of Sb and Sn in 0·5 *M* H_2SO_4 were traced to the presence of As, and the polarographic characteristics of Sb in the presence and absence of As and those of As itself were investigated. Tervalent As was found to give a smoothly sloping line instead of the normal step, and hence the polarogram of Sb in the presence of As^{III} consisted of a step with a considerable slope. As the Sb must be retained as Sb^{III}, oxidation of the As to As^{V} is not permissible, but it was found that a correction could be applied to the Sb step-height by regarding the arsenic polarogram as a gradient linearly related to the concn. In the medium used for the determination of Sn (0·5 *M* H_2SO_4 - 10 *M* HCl, 3:2), As^{V} is not polarographically reducible. Tervalent As gives a well-defined step almost coincident with that of Sn and, since a well-defined step is obtainable equally well from Sn^{II} or Sn^{IV} soln. in this medium, the interference of As can be removed by a suitable oxidation procedure. Such an oxidation procedure with $KClO_3$ and HCl is described.

A. O. JONES

2054. **Determination of niobium in the presence of large amounts of titanium by the method of oscillographic polarography.** Ya. P. Gokhshteĭn (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1956, **22** (1) 38–44.—The reduction of Ti^{IV} and Nb^{V} at the dropping-mercury electrode in H_2SO_4 solutions is studied. In 23 *N* H_2SO_4, single polarographic waves are given by Ti with a $E_{\frac{1}{4}}$ of + 0·04 V *vs.* the S.C.E. and by Nb with a $E_{\frac{1}{4}}$ of − 0·63 V *vs.* the S.C.E. The wave height with Nb is linearly related to the concn. Small amounts of Ti increase the height of the niobium wave, but large amounts reduce it. A nomogram showing the relations between diffusion current and concn. of Ti and Nb is constructed.

G. S. SMITH

2055. **Chemistry of niobium and tantalum. XVI. Photometric determination of niobium as peroxy compound.** H. Schäfer and F. Schulte (Inorg. Chem. Inst., Univ. Münster, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 73–85.—The photometric method (Klinger and Koch, *Ibid.*, 1943, **126**, 269), in which Nb^{V} and Ta^{V} are treated with H_2O_2 in conc. H_2SO_4 and the extinctions at 365 and 283 mμ, respectively, are measured, is examined in detail. Interference by Ti, Sn, W and Fe is avoided by conversion into the chlorides and sublimation; $TiCl_4$ and $SnCl_4$ volatilise first and pure $TaCl_5$ and $NbCl_5$ sublime. The influence of the concn. of H_2O_2 and H_2SO_4 is investigated. Niobium is determined photometrically in the presence of Ta by the use of a correction factor derived by determining the sum of Nb_2O_5 and Ta_2O_5. The accuracy of the method is within about $\pm$ 0·5 per cent.

J. P. STERN

2056. **Spectrophotometric determination of niobium and tantalum in alloy steel.** Masao Yana, Heiichi Mochizuki, Rokuro Kajiyama and Takeshi Misaki (Nippon Yakin Kogyo Co. Ltd., Daishigawara, Kawasaki). *Japan Analyst*, 1955, **4** (8), 499–505.—The application of the colorimetric determination of Nb and Ta with pyrogallol (**I**) (Krivoshlykov *et al.*, *J. Appl. Chem.*, U.S.S.R., 1937, **10**, 184) to the analysis of alloy steel and ferroniobium was studied with reference to the separation of

W, Si and Ti. Tungsten is removed by extracting an ignited (600° to 800° C) insol. residue, obtained by the decomposition of the sample with aqua regia and $HClO_4$, with dil. alkali soln. Silicon is removed with HF. The separation of Ti is too difficult and the colorimetry is carried out in its presence. *Procedure*—The sample (1 g) is dissolved in aqua regia (20 ml), then treated with $HClO_4$ (20 ml), cooled and dissolved in 0·5 *N* HCl (200 ml). The soln. is boiled for 5 min. with Na_2SO_3 (5 g) and filter-paper pulp, then filtered and the residue is washed with HCl (2 per cent.) and ignited at 600° to 800° C. The residue is extracted with NaOH (1 per cent., 100 ml), filtered, washed with HCl (2 per cent.) and treated with H_2SO_4 and HF (4 per cent., 2 to 3 ml). The product is fused with $Na_2S_2O_7$ (5 g), extracted and made up to 100 ml with 4 per cent. ammonium oxalate (**II**). A portion (Nb $\simeq$ 0·1 mg) is diluted to $\simeq$ 50 ml with **II**, treated with $Na_2S_2O_3$ (20 per cent., 10 ml) and **I** (30 per cent., 30 ml) and made up to 100 ml with **II**. The extinction is measured at 430 mμ. Another portion (Ta $\simeq$ 0·5 mg) is treated with H_3PO_4 (1 + 4) (10 ml) and **I** (30 per cent., 30 ml) and made up to 100 ml with **II**; the extinction is measured at 430 mμ. When Ti is present, the extinction of the H_3PO_4 soln. is also measured at 500 mμ and both Ti and Ta are calculated by means of an experimentally derived equation; the amount of Nb is deducted from the result for Ti. The results agree well with those by gravimetric analysis.

K. Saito

2057. **Protoactinium. I. Analytical separations.** J. Golden and A. G. Maddock (Radiochemical Lab., Cambridge, England). *J. Inorg. and Nuclear Chem.*, 1956, **2** (1), 46–59.—The determination of ^{231}Pa in heavy-metal sulphates in the presence of silica, or in uranyl salts, consists in the separation of Pa (yields $\not<$ 80 per cent.) from Ca, Ba, Pb, Al, Ti, V, Mn, Fe, Cr, Ta, Zr, Po, Th or U by a suitable combination of the steps given below, followed by α-scintillation counting of an aliquot or a slurry evaporated on an inert foil at a surface density of 1 mg per sq. cm. (*a*) Co-precipitation with BaF_2 (as $BaPaF_7$) from an aq. soln. of 10 mg of Ba per ml with 2·5 *N* HF (or 5 *N* NH_4F), or with MnO_2 from HNO_3 soln. The Pa is re-dissolved in HF, HCl or HCl - $AlCl_3$. (*b*) Extraction from 6 to 8 *N* HCl into an equal volume of di*iso*propyl ketone, possibly as $PaCl_5.3(C_3H_7)_2CO$. (Less efficient substitutes are di*iso*propyl carbinol or *iso*butyl methyl ketone.) Fluoride ions must be masked by excess of $AlCl_3$. The organic solution slowly deposits Pa on the polyethylene container. (*c*) Back-extraction from the solvent into 6 to 8 *N* HCl - 0·5 *N* HF. Aqueous samples containing Pa are stabilised by HCl or HF and are handled in polyethylene apparatus. There is no loss of Pa during the evaporation of aq. soln. or during the subsequent removal of ^{210}Po by ignition of residual solids at 800° C.

E. N. Jenkins

2058. **Continuous analysis of trace amounts of oxygen in gases.** F. W. Karasek, R. J. Loyd, D. E. Lupfer and E. A. Houser (Phillips Petroleum Co., Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 233–236.—A continuous oxygen analyser for determining from 1 to 1000 p.p.m. (by vol.) of O in process gases, *e.g.*, N, C_2H_4, butadiene, etc., is described and illustrated. In the apparatus, the O in the sample continuously and rapidly oxidises a dil. alkaline soln. of sodium anthraquinone-2-sulphonate, the change to the colourless diketo form being proportional to the amount of O present. A closed-cycle pumping system ensures that the partly oxidised reagent is passed into a photocell where its optical transmittance is measured. The reagent is then returned to the regenerator (zinc amalgam) in which it is completely reduced to the red dihydroxy form, the optical transmission of which is measured in a reference photocell before the soln. is passed into the reactor again. The content of O in the gas is calculated from the differential extinction between the completely reduced soln. and the partly oxidised soln., the standard calibration curve and the capillary-leak calibration curve being utilised. Reaction contaminants in the gas, *e.g.*, CO_2, H_2S and CS_2, should be removed initially in a scrubber. The useful life of the reagent varies from two weeks to six months.

W. J. Baker

2059. **Quantitative determination of sulphur and silicon by means of a steeloscope.** A. S. Andrianov, V. N. Razvodovskaya and P. M. Sinekaeva. *Uch. Zap. Saratov. Univ.*, 1954, **40**, 107–114; *Ref. Zhur., Khim.*, 1955, Abstr. No. 23,980.—Conditions for determining S (0·04 to 1 per cent.) in solutions, and Si (2·5 to 9·5 per cent.) in aluminium alloys by means of a Sventitskiĭ activated a.c. arc and a steeloscope are described.

G. S. Smith

2060. **A spectrophotometric method for the determination of sub-micro quantities of sulphur with 4-amino-4′-chlorodiphenyl.** A. S. Jones and D. S. Letham (Chem. Dept., The University, Birmingham, England). *Analyst*, 1956, **81**, 15–18.—4-Amino-4′-chlorodiphenyl has been used to determine 30 to 120-μg amounts of SO_4''. To determine inorganic SO_4'', an excess of the reagent in 0·1 *N* HCl is added to the soln. at pH 2 to 7 and the ppt. is removed by centrifuging. An aliquot of the supernatant liquid, suitably diluted, is examined spectrophotometrically at 254 mμ (ϵ = 22,090). From the difference in extinction before and after pptn. the amount of reagent removed in the ppt. is calculated and hence the content of SO_4''. When present, PO_4''' are removed by addition of a controlled excess of magnesia mixture. To determine S in organic compounds, the sample ($\equiv$ 20 to 50 μg of S) is oxidised with conc. HNO_3 in a sealed tube at 280° C. After removal of HNO_3 by evaporation, and solution of the residue in HCl, the procedure is as already described. Recovery of SO_4'' is within 1 per cent. of theoretical and within 2 per cent. when removal of PO_4''' is necessary. Recovery from organic compounds (mercaptals of thioglycollic acid) is within 2 per cent.

A. O. Jones

2061. **Precipitation of sulphides from homogeneous solutions by thioacetamide.** E. H. Swift and E. A. Butler (California Inst. Technol., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 146–153.—A kinetic study of the hydrolysis of thioacetamide (**I**) in acid aq. soln. is reported, and the application of the results to the pptn. of the H_2S group of metals in analysis is discussed, with special reference to data for PbS. The hydrolysis of **I** to acetamide (**II**) and H_2S in dil. acid soln. at 90° C is first-order with respect to the concn. of **I** and H^+; only $\simeq$ 5 per cent. of **II** is hydrolysed to acetic acid and NH_3. It cannot be assumed that **I** hydrolyses rapidly and quant. in hot acid soln. and that it can be used instead of H_2S without modifying

the usual procedure. The pptn. of PbS by hydrolysis of **I** is incomplete under conditions that are satisfactory with gaseous H_2S; between 60° and 90° C the reactions are complicated by processes that change with the pH (1 to 5) of the soln. It is, however, possible to control the rate of pptn. of sulphides by **I**, and also to effect separations that depend on variations in the rates of the direct reaction between **I** and metal ions. W. J. BAKER

2062. **The heterometric micro-determination of sulphuric acid as barium sulphate. A general study.** M. Bobtelsky and J. Eisenstadter (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (2), 186–193.—Sulphate is titrated by the heterometric method (*cf. Anal. Abstr.*, 1954, **1**, 51) under the following conditions. *Procedure*—To 5 ml of soln., containing a few mg of SO_4'', add 1 ml of 2 *N* HCl and 5 ml of ethanol, and titrate with 0·01 to 0·02 *M* $Ba(NO_3)_2$ in 50 per cent. ethanol. The max. error is 3 per cent. The following ions interfere when present in a molar ratio of > 3 to 1—PO_4''', NO_3', Fe^{+++}, Cr^{+++}, K^+. W. C. JOHNSON

2063. **The titrimetric determination of sulphate with 4-amino-4′-chlorodiphenyl hydrochloride as reagent.** R. Belcher, A. J. Nutten, E. Parry and W. I. Stephen (Chem. Dept., The University, Birmingham, England). *Analyst*, 1956, **81**, 4–8.—The use of 4-amino-4′-chlorodiphenyl hydrochloride as a reagent for the titrimetric determination of SO_4'' has been investigated. The reagent has some disadvantages, including low solubility, non-selectivity and certain difficulties in ensuring complete reaction between the ppt. and the alkaline titrant, but it is highly sensitive to SO_4'' and under the conditions described 25 to 100 mg of SO_4'' in an initial vol. of 100 ml and 2·5 to 25 mg in an initial vol. of 50 ml can be determined. Zinc, Cu, Mg, Fe^{+++}, Cr^{+++}, Ca and the alkali metals do not interfere when present in moderate amounts. Interference by Al can be overcome by addition of tartaric acid. Tellurite and selenate (but not tellurate and selenite) interfere and PO_4''' must be removed as $Mg(NH_4)PO_4$. A. O. JONES

2064. **A rapid volumetric determination of sulphates of ammonium, sodium and potassium by the use of sodium rhodizonate test-paper as external indicator.** Tomoyuki Mukoyama (Faculty of Eng., Yanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1955, **4** (9), 558–563.—Sulphate ions can be titrated in a neutral or an acetic acid soln. with 0·3 *N* $BaCl_2$ at $> 60°$ C, with sodium rhodizonate test-paper as external indicator. Acetate, chloride (less than the amount of the SO_4'') and NH_4^+ (less than an equiv. amount of the SO_4'') do not interfere; NO_3' should be absent. The sample (0·5 g) is dissolved in water, neutralised with acetic acid to methyl red and titrated with 0·3 *N* $BaCl_2$. The Ba^{++} soln. is at first added quickly (10 to 15 ml per min.). Near the end-point one drop of the soln. is tested on the indicator paper; when this turns red the excess of Ba^{++} is titrated with 0·3 *M* $(NH_4)_2SO_4$ until the indication becomes negative. The relative error is $< 0·3$ per cent. compared with the result of the gravimetric analysis. K. SAITO

2065. **Kinetic methods of quantitative analysis. II. Determination of thiosulphate and copper.** K. B. Yatsimirskiĭ (Ivanovo Chem.-Tech. Inst.). *Zhur. Anal. Khim.*, 1955, **10** (6), 344–348.—The reaction of thiosulphate with ferric ion, which is catalysed by Cu^{++}, is studied. Ferric chloride soln. (5 ml of 0·00233 *M* with sufficient HCl to make the soln. 0·0033 *N* in HCl after the subsequent additions), 10 ml of 0·242 *M* KSCN and varying amounts of 0·004 *M* $Na_2S_2O_3$ were diluted to 50 ml in a calibrated flask, the soln. was transferred to a photometer cell and the change in extinction was measured at intervals of time until the reaction was half completed. Experiments were also carried out in the presence of Cd^{++} (a calculation of the instability const. of CdS_2O_3 confirmed the value of Denney and Monk, *Trans. Faraday Soc.*, 1951, **47**, 992) and Cu^{++}. On the basis of the theoretical considerations in an earlier paper (*Anal. Abstr.*, 1956, **3**, 1967) it is shown that in the absence of Cd^{++} and Cu^{++} the equilibrium concn. of $S_2O_3'' = 0·0083\,y\frac{1}{t}$, where y is the slope of the graph of time - log extinction. The equation is confirmed experimentally. The concn. of Cu^{++} to give a 10 per cent. increase (the min. definitely ascertainable increase) is 0·4 μg per 10 ml. G. S. SMITH

2066. **Method of analysis of the system sulphuryl chloride, chlorosulphonic acid and sulphur trioxide.** É. M. Natanson, A. A. Shokol and A. S. Rabinovich (Inst. Gen. and Inorg. Chem., Acad. Sci., Ukrain. SSR). *Zavod. Lab.*, 1955, **21** (12), 1439–1443.—The composition of a mixture of SO_2Cl_2, $ClSO_2OH$ and SO_3 can be calculated from the total sulphur and chlorine contents, and the S present as $ClSO_2OH$ and SO_3. *Determination of total S and Cl*—In a cylinder with a ground glass stopper, 200 ml of 0·1 *N* NaOH or 200 ml of warm (40° to 50° C) water and an ampoule containing 2 to 3 g of the ternary mixture are shaken together for 2 to 3 hr. The contents are transferred to a 500-ml calibrated flask, the solution is made up to the mark, and the Cl' and SO_4'' are determined by the usual methods. *Determination of S in the form $ClSO_2OH$ and SO_3*—The ternary mixture (3 to 4 g) in an ampoule and a mixture (1 : 1·5) of NaH_2PO_4 (dried at 130° to 135° C) and KCl in the proportion of 7 to 9 g per 1 g of sample are placed in a 200 to 300-ml cylinder with a ground glass stopper. The ampoule is broken and the mixture is shaken for 15 to 20 min. After 10 to 12 hr. or on the following day the cylinder is opened and kept at 110° to 120° C for 3 hr. The mixture is treated with 50 ml of pure chloroform, then shaken for 10 to 15 min. and kept at 110° to 120° C for 60 min. The contents of the cylinder are then dissolved in water and the solution is transferred to a 500-ml calibrated flask. Sulphur is determined gravimetrically by the usual method. G. S. SMITH

2067. **Determination of total sulphur in pyrites by an ion-exchange method followed by alkalimetric titration.** Shizo Hirano and Moriji Kurobe (Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1955, **4** (9), 552–554.—Sulphur in pyrites is oxidised to sulphate by fusing with Na_2O_2 in a nickel crucible. The product is extracted with water and passed through a column of cation-exchange resin. The resulting H_2SO_4 is titrated with alkali, with a mixture of methylene blue and methyl red as indicator. The presence of Al, Fe, Si and small amounts of Se, Te, P and As does not vitiate the determination. When the amount of P or As is $> 0·05$ per cent., the sum of S, P and As is titrated as described above, and titration of the resulting soln. is then continued, but with phenolphthalein as indicator. When Pb or Ba, which produces insol. sulphate, is present, the addition of Na_2CO_3 to the

Na_2O_2 is advantageous. *Procedure*—The sample (0·3 to 0·7 g) is fused with Na_2O_2 (5 g) in a nickel crucible and the melt is extracted with water (100 ml). The soln. is boiled for 1 min. (to decompose H_2O_2) and made up to 200 ml. A 50-ml portion taken from the supernatant liquid is passed through a column of Amberlite IR-120 (H). The column is washed with water (100 ml). The eluate and the washings are bubbled with air free from CO_2 and titrated with NaOH (0·1 *N*). K. SAITO

2068. **Determination of total sulphur in cements, pigments and rubber articles by an ion-exchange method followed by alkalimetric titration.** Shizo Hirano, Moroji Kurobe and Fumio Ito (Inst. of Techno-anal. Chem., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1955, **4** (9), 565–568.—The total S in cements (< 1 per cent.) is rapidly (< 1·5 hr.) determined by converting it into sulphate, which is submitted to ion exchange and alkalimetric titration. The sample (0·5 to 0·7 g) is fused with Na_2O_2 and Na_2CO_3 (1 + 1) (8 g), then extracted with water and made up to 200 ml. A 50-ml portion is treated with Amberlite IR-120 (H) in a separating funnel (to remove most of the CO_2) and then passed through a column of the resin. The eluate is bubbled with air (free from CO_2) and titrated with 0·02 *N* NaOH. For the analysis of pigments, including ZnS, CdS, HgS and ultramarine, the sample (0·4 to 0·7 g) is fused with Na_2O_2 (5 g), extracted with water and similarly titrated with 0·1 *N* NaOH. For the analysis of S in rubber articles, the sample (0·1 to 0·5 g) is mixed with Na_2O_2 (2 to 5 g) and a small piece of filter-paper is placed on the surface and ignited. The sample is thus instantaneously fused and the conversion of total S into SO_4'' is effected. The cake is leached with water and similarly titrated. When other acidic elements such as As or P are present, the sum of SO_4'', AsO_4''' and PO_4''' is determined by a titration to methyl red, followed by a further titration to phenolphthalein for PO_4''' or AsO_4'''. K. SAITO

2069. **Argentimetric method for determination of selenium.** H. Hahn and U. Viohl (Inorg. Chem. Inst., Univ. Kiel, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 40–42.—Quantitative pptn. of Ag_2Se is effected by reducing solutions containing SeO_3'' with hydrazine sulphate in aq. H_2SO_4 in the presence of a known excess of $AgNO_3$, the $AgNO_3$ being back-titrated with NH_4SCN; SeO_4'' must first be reduced to elementary Se, which in HNO_3 gives SeO_3'' used in the determination. The presence of Te does not cause interference, and 20 to 40 mg of Se are determined to within ± 0·1 per cent. *Procedure*—Heat the selenium solution (approx. 0·05 *M*) to dryness with conc. H_2SO_4 (2 to 3 ml) to remove nitrogen oxides and then dilute with water to a vol. of 50 to 100 ml. First add 0·1 *N* $AgNO_3$ in excess and then, to the almost boiling solution, solid hydrazine sulphate, more being added at 5 to 10-min. intervals until the ppt. coagulates and the solution appears clear (after about 1 to 2 hr.). To the cold mixture add 2 *N* HNO_3 (10 ml per 50 ml of solution) and saturated $FeNH_4(SO_4)_2$; back-titrate the excess of $AgNO_3$ with 0·1 *N* NH_4SCN. J. P. STERN

2070. **Quantitative determination of impurities in selenium.** G. E. Peterson and E. W. Currier (Fed. Telecomm. Lab., Nutley, N.J., U.S.A.). *Applied Spectroscopy*, 1956, **10** (1), 1–4.—A quant. rapid spectrochemical procedure, in which a large Littrow quartz spectrograph is used, is described for the determination of Al, Bi, Cu, Pb, Mg, Ni, Ag and Zn at a nominal range of 1 to 100 p.p.m. in high-purity Se. A 0·5-g sample is introduced into a cup electrode and melted by passing current through a nichrome coil surrounding the electrode. A solution of Pd is dried in the same electrode by i.r. heating to act as internal standard. The electrodes are burned as the anode in a d.c. arc at 5 amp., an efficient air flow being maintained round the arc stand to remove obnoxious fumes and to prevent absorption of the incident light by these vapours. The average percentage error is ± 20 per cent. calculated from the average of triplicate determinations. Standards can be prepared easily with the minimum of contamination by the use of a 0·05-ml portion of a solution containing the elements sought as impurities together with pure Se. The spectral lines used and the minimum detectable amounts of each element are tabulated. K. A. PROCTOR

2071. **Isotopic analysis of polonium-208 - 209 mixtures.** D. J. Hunt and G. Pish (Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (2), 87–91.—To reduce toxicity risks associated with Po isotopes and to preserve the samples for other studies, a spectroscopic method has been developed in which the sample is excited in a quartz tube by an electrodeless discharge. Band spectra of $(^{208}Po)_2$ and $(^{208}Po^{209}Po)$ are resolvable with a 3-metre-grating spectrograph and the ratios of the two isotopes are derived from measurements of the intensity ratios of the band heads due to the two molecules. The minimum quantity of sample needed to fill the tube (25 mm long, 1 mm diameter) at 3·2 mm pressure at 525° C is 20 μg. From a single spectrogram the probable error of the result is ± 6 per cent. B. S. COOPER

2072. **The separation of molybdenum [of different] valencies by paper chromatography. II.** H. M. Stevens (Long Ashton Res. Sta., Univ. of Bristol, England). *Anal. Chim. Acta*, 1956, **14** (2), 126–130.—The prep. of 8-hydroxyquinoline complexes of Mo^{VI} and Mo^{V} is described and their absorption spectra in the visible and u.v. range are shown. The R_F values of the complexes obtained on paper with the use of ethanol as eluent are, for Mo^{VI}, 0, and for Mo^{V}, 0·9 to 1·0, but separation is not quant. The prep. of a soln. of Mo^{III} in aq. HCl is described. Separation of Mo^{III} from Mo^{V} is effected on paper strips with the use of a soln. of thiocyanic acid in ether (R_F for $Mo^{III} = 0$, for $Mo^{V} = 0·8$ to 0·9). Further expt. suggest that Mo^{III} does not form a stable thiocyanate or oxine complex. (See also *Anal. Abstr.*, 1956, **3**, 1702.) W. C. JOHNSON

2073. **Volumetric method of determining molybdenum based on its reduction in a bismuth reductor.** E. B. Ankudimova. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 197–206; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,461.—In HCl (1·0 to 1·5 *N*) Mo^{VI} is quant. reduced in a bismuth reductor to Mo^{V}. The solution is titrated with permanganate and vanadate. G. S. SMITH

2074. **Use of ion-exchange chromatography for determining molybdenum in steels and ores.** I. P. Alimarin and A. M. Medvedeva (M. V. Lomonosova Moscow Inst. of Fine Chemical Technology). *Zavod. Lab.*, 1955, **21** (12), 1416–1418.—Molybdenum as

permolybdic acid can be separated from Fe in slightly acid soln. by means of a cationite. Of a number of cationites tested, SBS was found to have the lowest reducing action. The SBS resin (10 g), having a grain size of 0·5 to 1 mm, is first treated with 10 per cent. HCl and then with H_2O in a column 1 cm in diameter. In 0·5 *N* H_2SO_4 in the presence of H_2O_2 no adsorption of Mo occurs, whilst Fe is completely adsorbed. In HCl soln., permolybdic acid is unstable and Mo and Fe cannot be separated by means of SBS. In the absence of H_2O_2, Mo is adsorbed from H_2SO_4 soln.; at pH 5·5 to 6·0, 75 per cent. is adsorbed, but, in 0·1 to 0·5 *N* H_2SO_4, 95 to 99 per cent. is adsorbed. To separate Mo and Fe, a solution containing 1 per cent. of H_2O_2 and 0·1 *N* in H_2SO_4 is passed through the column at the rate of 3 ml per min. Copper, Ni, Mn and small amounts of Ti (6 to 7 mg) behave like Fe; W and V behave like Mo. G. S. SMITH

2075. **Determination of uranium, especially in shale and kolm.** K. Käärik (Royal Inst. Tech., Stockholm, Sweden). *Suomen Kem., B.* 1956, **29**, 1–2.—The use of $HClO_4$ with the HNO_3 and nitrates for dissolving samples of Swedish alum shale and kolm before uranium extraction with ether is described. Swedish alum shale and the mineral kolm contain 0·005 to 0·03 and 0·05 to 0·4 per cent. of U (in the acid-soluble form) and 10 to 35 and 20 to 70 per cent. of organic matter, respectively. *Method* (*i*)—Shale (5 g) is dissolved by boiling with a mixture of HNO_3 (15 to 20 ml) and $HClO_4$ (70 per cent., 25 to 30 ml). After dilution, the residue is filtered off and the soln. is evaporated to dryness. The salts are dissolved in HNO_3; ammonium or sodium nitrate is added and U is extracted with ether. Kolm (0·5 g) is oxidised similarly, but with a few tenths of a gram of $NaNO_3$ added to aid dissolution of phosphates. *Method* (*ii*)—The sample of uranium mineral, silicate, roasted shale or kolm is dissolved in a mixture of $HClO_4$, HNO_3 and HF in a platinum dish. The soln. is evaporated twice to dryness and the salts are treated and extracted as above. The polarographic determination of the ether extract is described.
O. M. WHITTON

2076. **Neutron activation analysis with the van de Graaf accelerator. Application to the halogens.** G. J. Atchison and W. H. Beamer (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 237–243.—A rapid method of analysis for milligram amounts of F and microgram amounts of the other halogens is based on neutron activation. The neutron source is the nuclear reaction $^9Be(d,n)^{10}Be$, deuterons accelerated at 2 meV being used. Metal foil (evaporated Ag or In films mounted on polystyrene film) was used to determine the available neutron flux. An apparatus for the automatic irradiation and measurement of radioactivities having half-lives of the order of 10 sec. is described. Interference is caused by Cl, Br and I in the determinations of any one of the three elements; Cl could be determined in the presence of the other two elements if the activity of the 2·1- and 1·6-meV γ-rays from ^{38}Cl were to be measured. Owing to its short half-life ^{20}F does not interfere in the determination of the other three halogens.
D. G. HIGGS

2077. **Voltammetry of silver halide suspensions and amperometric titration of halides.** I. M. Kolthoff and J. T. Stock (Sch. Chem., Univ. Minnesota, Minneapolis, Minnesota, U.S.A.). *Analyst*, 1955, **80**, 860–870.—The voltammetric behaviour of silver halides was studied systematically with a rotating platinum electrode. In a colloidal or flocculated suspension of silver halide the electrode becomes coated with a film of the halide, which varies in thickness with the conditions. Reduction of these films at the appropriate potentials interferes with the development of the limiting current of free silver ions. This film formation is prevented by the presence of gelatin which is adsorbed on the silver halide particles. To obtain normal titration graphs, amperometric titrations of halides with $AgNO_3$ must be made in the presence of gelatin.
A. O. JONES

2078. **Azo dyestuffs as organic reagents. II. Detection of fluorine with zirconium 4-(*p*-dimethylaminophenylazo)diphenylarsinate.** Kiyo Tsuji and Mayumi Kageyama (Japan Women's Univ., Takatatoyokawa-cho, Bunkyo-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (11), 1184–1186.—A filter-paper is successively impregnated with 4-(*p*-dimethylaminophenylazo)diphenylarsinic acid [0·025 per cent. in a mixture of ethanol and HCl (9 + 1)], Zr soln. [0·1 per cent. $Zr(NO_3)_4$ in *N* HCl,] cold 2 *N* HCl and warm (50° C) 2 *N* HCl, and washed with water, ethanol and ether. Fluoride ions (> 0·05 μg in *N* HCl) change the brown colour of the test paper to red. Common cations and anions, including oxalate, PO_4''', AsO_4''', SO_4'' and S_2O_3'' (<100 times the weight of the F′), which vitiate Feigl's method, do not interfere with the detection of more than 4 μg of F′.
K. SAITO

2079. **Separation of fluoride ions by the use of ion-exchange resin.** Wataru Funasaka, Makoto Kawase, Tsuguo Kojima and Yoshifumi Matsuda (Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1955, **4** (8), 514–517.—A small amount of F′ (0·05 to 2 mg) is separated from other anions that interfere with its colorimetric determination by the use of the anion-exchange resin Amberlite IRA-410(OH). The sample soln. is passed through a cation-exchange resin to replace all the cations with H^+. The acid soln. is passed through Amberlite IRA-410 (100 mesh; diameter 7 mm; length 15 cm; rate of flow, 1 ml per min.); no significant break-through of F′ is observed in the presence of 0·5 milli-equiv. of other anions. The column is eluted with 0·1 *N* NaOH (< 100 ml). The elution also takes place satisfactorily when F′ are adsorbed in the form of SiF_6'', presumably owing to the decomposition of SiF_6'' with NaOH. When the amount of F′ is > 0·1 mg per ml, the Cl form of the resin can also be used and the column eluted with NaCl soln.
K. SAITO

2080. **Investigation of fluorspar and a proposed German standard method for its analysis.** F. Specht (Bayer A.-G., Leverkusen, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 85–96.—Methods for the determination of CaF_2 in fluorspar are reviewed, together with their likely sources and limits of error. The method proposed as a German standard involves either titration with EDTA (disodium salt) or the classical pptn. of Ca oxalate followed by redissolution in H_2SO_4 and titration with $KMnO_4$. Procedures for the determination of SiO_2, $BaSO_4$, Fe and Al (as R_2O_3), Mg (as $Mg_2P_2O_7$), Pb (as $PbSO_4$), and Zn (as ZnS) are also detailed.
J. P. STERN

2081. **Photometric determination of bromine as tetrabromofluorescein.** F. A. Pohl (A.E.G. Lab., Belecke, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 68–73.—Traces of Br′ in the presence of larger quantities of Cl′ in semi-conductors are determined by reaction with chloramine T and fluorescein. Results are dependent on pH and are affected by excess of reagents and time of reaction, so that for satisfactory reproducibility strict adherence to conditions specified is essential. Iodides interfere. The accuracy is not specified. *Procedure*—Dilute the neutral or weakly acidic sample to 5 ml, add 1 ml of acetate buffer (pH 5·5) and 1 ml of 0·003 per cent. fluorescein (in 0·0025 *N* NaOH) and shake. Allow 1 ml of 0·1 per cent. aq. chloramine T to react with this solution for exactly 3 min., then stop the reaction by adding 0·1 ml of 5 per cent. NaOH (containing 0·5 per cent. $Na_2S_2O_3$). Dilute to 10 ml and determine the extinction at 525 mμ in 2·0-cm cells, against a blank prepared with NaCl solution. J. P. Stern

2082. **Detection of bivalent manganese by oxidation in alkaline medium.** M. P. Babkin. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 136–140; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,463.—In the test for Mn^{II} by oxidation in alkaline soln. with bromine water or persulphate there is no interference from NH_4^+, K^+, Na^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Al^{+++}, Fe^{III}, Fe^{II}, Zn^{++}, Co^{++}, Ni^{++}, Cu^{++}, Cd^{++}, Bi^{+++}, Hg^{II}, Hg^{I}, Pb^{++}, Sb^{+++} and Ag^+ in concn. of 100 mg per ml. In the presence of Cl′, which interferes, several drops of the soln. are treated with NaOH soln. and 1 or 2 drops of 3 per cent. H_2O_2 soln. and boiled. The ppt. is filtered off and washed, and part of the ppt. in a test-tube is boiled with NaOH and bromine water or $(NH_4)_2S_2O_8$. After the ppt. has settled, the colour of the soln. is observed. The min. amount detectable is 0·5 μg of Mn per ml. G. S. Smith

2083. **Determination of bivalent manganese by means of oxalic acid.** A. Kh. Batalin and L. V. Sadovskaya. *Vestnik Khim. Obshch. im. D. I. Mendeleeva, Chkalovskoe Otd.*, 1954, (5), 19–22; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,462.—To detect Mn^{II}, 1 ml of the solution is shaken with 2 drops of 25 per cent. NaOH soln. and *N* oxalic acid is added dropwise. The ppt. dissolves to give a raspberry-red soln. The complex with oxalic acid starts to form at pH ≃ 7. The min. amount detectable is 6 μg of Mn per ml, and the limiting dilution is 1 in 200,000. Most of the usual cations do not interfere and do not lower the sensitivity. Interference is caused by reducing agents, *e.g.*, Fe^{II}, $Fe(CN)_6^{''''}$ and $SO_3^{''}$, and large amounts of Co. Tartrate, citrate, $K_4P_2O_7$, NH_4Cl, NaF, sodium acetate, Na_2HPO_4, Na_2CO_3 and ammonium carbonate do not interfere. G. S. Smith

2084. **The determination of manganese with sodium bismuthate. I. A new colorimetric determination in sulphuric acid containing silver nitrate.** Hisashi Kiyota and Toshio Yamamoto (Kyoto Gakugei Univ., Kamigyo-gu, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1179–1183.—When a small amount of Mn (1 to 6·5 g) is treated with sodium bismuthate (0·05 g) in an H_2SO_4 soln. (≃ 3 *N*, 100 ml) containing $AgNO_3$ (10 per cent., <0·1 ml) at < 40° C, Mn is instantaneously oxidised to $KMnO_4$ and the excess of bismuthate can be readily decomposed by subsequent heating at 70° to 90° C for > 2 min. The solution is cooled and colorimetrically determined by the usual method. The $KMnO_4$ remains unchanged throughout the subsequent heating and standing for up to 4 hr. The modified method shortens the time taken for estimation, since the filtration can be eliminated. K. Saito

2085. **Determination of manganese in glass by surface treatment.** L. I. Ganago and N. A. Tananaev (Ural Polytech. Inst., Sverdlovsk). *Zhur. Anal. Khim.*, 1955, **10** (6), 378–379.—The sample of glass is attacked with HF confined within a ring of paraffin wax on the clean surface, the soln. is transferred to a small cylinder, boiled with dil. H_2SO_4 to clarify, and then with ammonium persulphate and $AgNO_3$, and the colour is compared with that of a standard by adding water to the more intensely coloured soln. until the colours match. G. S. Smith

2086. **Spectrophotometric determination of iron with pyrogallol.** Masao Yana, Heiichi Mochizuki, Rokuro Kajiyama and Takeshi Misaki (Nippon Yakin Kogyo Co. Ltd., Daishigawara, Kasaki). *Japan Analyst*, 1955, **4** (8), 505–508.—Ferric iron (< 1 mg) can be determined by the measurement of its extinction at 550 mμ in an aq. soln. (pH 7·0 to 7·8) containing Na_2SO_3 (20 per cent., 20 ml per 100 ml), ammonium oxalate (4 per cent., 10 ml) and pyrogallol (5 per cent., 5 ml for 100 ml). Under the given conditions, Nb, Ti and Mo fail to show any significant absorption at 550 mμ. Chromium and a large amount of Ni interfere, but this effect can be eliminated by the use of a working curve prepared in the presence of known amounts of Ni and Cr. K. Saito

2087. **Spectrophotometric determination of iron with 5-sulphoanthranilic acid.** J. M. Zehner and T. R. Sweet (Ohio State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 198–200.—A new method for the spectrophotometric determination of Fe^{+++} has been developed by the use of 5-sulphoanthranilic acid (**I**) buffered at pH 4·0. The colour formed between Fe^{+++} and **I** was found to vary with pH, but was almost constant over the pH range 3·6 to 4·4 with a very large excess of **I** and was stable within 1 per cent. for three days. A suitable wavelength for absorption measurements was found to be 455 mμ, where a plateau is present in the otherwise sloping absorption curve. Beer's law is obeyed over the range 5 to 150 p.p.m. of Fe^{+++}. Interference is caused by the coloured ions of Cr^{+++}, Co^{++} and Ni^{++}. Cuprous ions form a coloured complex with **I** that absorbs to a slight extent at 455 mμ. The intensity is decreased by Al^{+++} and $SO_4^{''}$, but Cd^{++}, Zn^{++} and Mn^{++} up to 12,500 p.p.m. and Pb^{++} up to 2250 p.p.m. do not interfere. D. G. Higgs

2088. **Chelatometry. IV. The decomposition product of Bindschedler's green as redox indicator. 1. Complexiметric determination of ferric salt.** P. Wehber (Mark A.-G., Hamburg-Wilhelmsburg). *Z. anal. Chem.*, 1956, **149** (3), 161–164.—The pale-brown decomp. product (**I**) of Bindschedler's green, formed by keeping its Zn double salt in light at 30° to 40° C, is a good redox indicator for the complexiметric titration of Fe^{III} salts at pH 2·5 to 3·5 with EDTA. With oxidising agents the indicator gives a green colour and the end-point is the change to orange. The method is particularly suitable for larger quantities of Fe^{III}, namely 10 to 250 mg

in 60 ml of solution, when accuracies within ± 1 to 0·1 per cent. are attained. *Procedure*—Adjust the pH of acidic $FeCl_3$ (about 50 ml) to about 1·5 to 2, add the indicator (80 mg of NaCl containing 1 per cent. of **I** and 0·1 per cent. of Safranine T) and acetate buffer (pH 3·5) (10 ml) and titrate with 0·1 *M* EDTA (disodium salt, of pH 5). After the first colour change, keep for 1 to 2 min., and if the colour reverts to green, complete the titration. Check the pH, which should be between 2·5 and 3·5.
J. P. STERN

2089. **Spectrophotometric determination of iron chelates.** D. G. Hill-Cottingham (Long Ashton Res. Sta., Bristol, England). *Analyst*, 1955, **80**, 906–908.—The chelates between $Fe^{\cdots}$ and EDTA, N-hydroxyethylethylenediaminetriacetic acid and diethylenetriaminepenta-acetic acid, (**I**), (**II**) and (**III**), respectively, are examined spectrophotometrically and a method is developed for their determination. The spectra depend very much on pH, but all three chelates have absorption peaks at ≃ 260 mμ. Soln. of **I** have max. absorption at 258 mμ within the pH range 2 to 6. For **II** and **III** the pH ranges are 2 to 3, and 3 to 7, for maxima at 262 and 260 mμ, respectively. *Procedure*—Standard series of the complexes are prepared from known amounts of Fe [$FeCl_3$, $Fe_2(SO_4)_3$ or $Fe(ClO_4)_3$] and a slight excess of the sodium salt of the chelating agent. The pH is adjusted with HCl to within the appropriate range and the extinctions are determined at the peak of the graph, with quartz cells and a water blank. The excess of chelating agent does not interfere. The soln. are photosensitive.
A. O. JONES

2090. **Volumetric determination of iron in the presence of copper.** M. N. Sastri and L. Subbaraya Sarma (Andhra Univ., Waltair, S. India). *Z. anorg. Chem.*, 1955, **281**, 221–224.—A rapid and accurate method of determining Fe in the presence of Cu is based on the photochemical reduction of Fe^{III} (Cu is not reduced) followed by titration of Fe^{II} with sodium vanadate soln. *Procedure*—To the soln. of the sample add an excess of 0·1 *N* sodium oxalate and dil. H_2SO_4 (1 + 6) and expose the mixture to bright sunlight for 15 to 20 min. Then add 5 ml of saturated aq. NaF soln. plus 0·5 ml of 0·1 per cent. diphenylbenzidine (as indicator), and titrate with 0·05 *N* sodium vanadate soln. to a blue end-point.
W. J. BAKER

2091. **Rapid volumetric method for estimation of iron in presence of interfering ions.** M. N. Sastri and C. Kalidas (Andhra Univ., Waltair, S. India). *Z. anal. Chem.*, 1956, **149** (3), 181–184.—The determination of Fe in ilmenite, chromite and other minerals by reduction with Na oxalate in bright sunlight and subsequent titration with sodium vanadate, with diphenylbenzidine as indicator, is described. No interference is caused by Cu, Cr, Ti, W, Mo, Mn, Co, Ni and F′; V interferes only slightly and gives high results. The method is accurate to within ±0·5 per cent. *Procedure*—Add 0·1 *N* Na oxalate (3 to 4 equiv.) and 6 *N* H_2SO_4 (10 ml) to the Fe solution and keep in bright sunlight for 15 to 20 min. until the yellow colour of the Fe oxalate complex disappears. Titrate with 0·05 *N* sodium vanadate, with diphenylbenzidine in syrupy H_3PO_4 (5 ml) as indicator, to a blue-violet end-point.
J. P. STERN

2092. **The masking of iron in determinations with EDTA (disodium salt).** I. Sajó (Iron Ind. Res. Inst., Budapest). *Magyar Kém Foly.*, 1956, **62** (1), 37–38.—Ferric iron is masked with sodium pyrophosphate. *Procedure*—If the metal to be determined is Ni, add to the soln. 10 per cent. sodium pyrophosphate soln. (50 ml) and 1 g of an indicator prepared from 1 pt. of murexide and 500 pt. of NaCl. Add aq. NH_3 until the yellow colour appears and then titrate with EDTA (disodium salt) (**I**). In the presence of Ca, Zn, Co, Mn, etc., add a soln. containing 10 mg of Ni, then aq. NH_3 (in the presence of Mn, use an excess of 5 ml) and titrate with **I**. The concn. of the required ion is obtained by subtracting the Ni content from the total vol. of **I** used. Aluminium can be masked similarly.
A. G. PETO

2093. **The analysis of metallic nickel. IV. Determination of iron.** Sigeru Yokosuka (Besshi Mine Office, Sumitomo Metal Mining Co. Ltd., Niihama). *Japan Analyst*, 1955, **4** (8), 509–512.—Iron in metallic nickel (> 0·0001 per cent.) is separated from Ni, Co, Cu and Zn by co-pptn. with Al (≃ 10 mg) in an ammoniacal soln. The ppt. is dissolved in HCl, reduced to the ferrous state and colorimetrically determined with 2:2′-dipyridyl. Manganese (< 0·5 per cent.) and Cr (< 0·05 per cent.) do not interfere. *Procedure*—The sample (5 g) is dissolved in HNO_3 (1 + 1) (100 ml) and diluted. An aliquot is successively treated with $Al^{\cdots}$ (10 mg), H_2O (50 ml) and aq. NH_3 soln. (1 + 1). The ppt. is filtered off, washed, dissolved in conc. HCl (10 ml) and re-pptd. The ppt. is dissolved in conc. HCl (10 ml), the soln. is evaporated, diluted to 20 ml with hot water, treated with aq. NH_3 soln. (1 + 1, 10 ml), 5 *N* acetic acid (15 ml), ammonium acetate (5 g) and hydroxylamine hydrochloride (10 per cent., 1 ml) and set aside for 15 min. 2:2′-Dipyridyl (0·1 per cent., 4 ml) is added, the soln. is made up to 100 ml and the extinction (520 mμ) is measured after 15 min. When > 60 μg of Fe are present, the addition of Al is not necessary.
K. SAITO

2094. **Spectrochemical analysis with a universal source unit. II. Determination of carbon in iron and steel.** Jiro Kashima and Kazuo Yasuda (Waseda Univ., Waseda, Tokyo). *Japan Analyst*, 1955, **4** (8), 482–486.—The ratio of the sum of the intensities of the spectral lines of C 2478·57 and Fe 2478·57 to the intensity of Fe 2480·16 was studied under various conditions of discharge, varying from an arc-like to a spark-like discharge. An optimum condition is obtained when the resistance is 6·5 ohms, the inductance 300 μH and the capacity 10 μF. The working curve is linear for the range 2 to 5 per cent. of C in cast iron (preliminary discharge 60 sec., exposure 60 sec.). Carbon in steel can be similarly determined when the content is > 0·2 per cent. (5·5 ohms; 400 μH; 40 μF; preliminary discharge 5 sec.; exposure 10 to 120 sec.). The texture of the cast iron appears to have a significant influence on the result. The average deviation from the mean is < 8·6 per cent.
K. SAITO

2095. **New photometric method for the rapid determination of the lead content of steel.** I. Bozsai and E. Kopócsy (Rákosi Mátyás Iron and Metalworks, Budapest). *Magyar Kém. Foly.*, 1956, **62** (1), 12–15.—Dissolve steel-shavings (1 g) in H_2O (40 ml) and 60 per cent. $HClO_4$ (8 ml) with gentle

warming, adding H_2O to keep the vol. constant. When solution is complete, add a few hundred mg of Pb-free steel-shavings (to remove Cu^{++}) and allow to stand for 3 min. Cool the soln., dilute it to 50 ml in a standard flask and filter. In a 10-ml graduated and stoppered test-tube, thoroughly mix conc. H_3PO_4 (5 ml), fresh gum acacia soln. (1 ml, prepared by dissolving 0·1 g of gum acacia in 6 ml of cold water) and the unknown soln. (2 ml). Dilute with water to 9 ml and, immediately before the determination, add 2·5 per cent. KI (1 ml); shake at once and determine the yellow PbI_2 against H_2O in a Pulfrich photometer, with a 1-cm cell and an S42 filter. In practice, the extinction of a steel with a gravimetrically determined lead content is measured and this is used to calculate the Pb in the unknown. Otherwise the following formulae can be used—mg of Pb per 10 ml of soln. = 0·18 × extinction, or percentage of Pb = 0·45 × extinction. The Pb-free steel must have an extinction <0·04. The accuracy is ± 0·02 per cent. The time required is 25 min. The metals usually present do not interfere, except for Cu^{++}, which is removed as described. A. G. PETO

2096. **Reaction for the cobalt cation.** E. Yu. Perel'man. *Vestnik Khim. Obshch. im. D.I. Mendeleeva, Chkalovskoe Otd.*, 1954, (5), 31–33; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,467.—Stable violet-coloured complexes are given by Co^{++} and alkali-metal pyrophosphates. The reaction with $K_4P_2O_7$ is more pronounced than that with $Na_4P_2O_7$. With an excess of $K_4P_2O_7$, cations of all the analytical groups, including those of V, Ti, W, Mo, Au, Ce and Pt, give colourless solutions. Exceptions are Cu and Cr; Cu^{++} gives a deep-blue and Cr^{+++} a green colour. At high concn. Ba gives a ppt., Ni^{++} gives a yellow-green soln. With Cu^{++} and Co^{++} together the colour is blue. The limiting dilution for detection of Co is 1 in 29,400, but in the presence of 15 times as much Cu and at 70° to 80° C the limiting dilution is 1 in 84,000. Soln. of the pyrophosphate complex of Co follow Beer's law. G. S. SMITH

2097. **Colorimetric determination of cobalt in zinc electrolytic solution with nitroso-R salt.** Tetsuo Katsura (Kosaka Kogyosho, Dowa Mining Co., Kosaka, Akita Prefecture). *Japan Analyst*, 1955, **4** (9), 574–577.—The colorimetric determination of Co with nitroso-R salt (**I**) was examined with reference to its use for factory control. The presence of Zn (< 20,000 times the weight of the Co) (10 per cent. in H_2SO_4), Cu (< 10 times), Ni (< 50 times), Mn (< 100 times), Fe (< 50 times) and Cd (< 100 times) does not vitiate the colorimetry when 5 ml of the reagent (5 per cent.) are added. By increasing the amount of **I**, allowable amounts of Cu, Mn and Fe are increased, but that of Ni is decreased. The electrolytic soln. (10 ml) (> 1 mg of Co per ml) is analysed by the usual method at pH 6·0. The residue (0·1 to 1 g), obtained on the purification of the electrolytic soln., is dissolved in aqua regia containing H_2SO_4, the soln. is heated to dryness, then extracted with dil. HCl and submitted to colorimetry. When the concn. of Cu or Cd is higher than permitted, H_2S is passed into an acidic sample soln. to ppt. the sulphide. K. SAITO

2098. **Photometric determination of cobalt in steel by means of the orange-red complex of cobalt salts with 2-nitroso-1-naphthol.** F. Jungblut (Aciéries Réunies de Burbach Eich-Dudelange Dommeldange, Luxembourg). *Chim. Anal.*, 1956, **38** (2), 49–54.—A rapid method of determining up to 21 per cent. of Co in steel depends on formation of the orange-red complex with 2-nitroso-1-naphthol (**I**) at 25° to 30° C in aq. NH_3. The vol. of the aq. NH_3 added is critical, the concn. of NH_3 being ≃ ten times that used by Yoe and Barton (*cf. Brit. Abstr. AI*, 1940, 394); this and the addition of ammonium citrate obviate interference by Fe. The accuracy is within ≃ ± 0·2 per cent., reproducibility is excellent, and one determination takes ≃ 40 min. *Procedure*—Dissolve the sample (0·1 g) in H_2SO_4 - H_3PO_4 (20 ml) plus conc. HNO_3 (1 ml), fusing any carbide residue with $K_2S_2O_8$. From the resulting soln. (filtered to remove SiO_2 and made up to 1 litre) transfer an aliquot (10 to 20 ml) to a 100-ml calibrated flask, heat to 25° C, add, with stirring, 20 ml of 25 per cent. w/v aq. ammonium citrate followed by 40 ml of fresh aq. NH_3 (d = 0·97) and then H_2O to within ≃ 2 cm of the mark. Then add, dropwise with stirring, 2 ml of a 0·125 per cent. w/v soln. of **I** in ethanol, fill to the mark with H_2O, stopper the flask and mix well. Keep the soln. for 10 min. at 25° C before measuring the extinction at 585 mμ in a rectangular cell (20 mm × 40 mm). The percentage of Co is calculated from one of three reference curves (< 3, 3 to 15, and 12 to 21 per cent. of Co, respectively). The procedure is also applicable to metal carbides containing 4 to 9 per cent. of Co. W. J. BAKER

2099. **Estimation of traces of cobalt in nickel and in nickel-iron alloys.** M. Pontet (Irsid, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1955, **37** (11), 372–374.—Cobalt is determined colorimetrically, in the presence of Ni and many other metals found in nickel alloys, as its complex with 2-nitroso-1-naphthol in toluene soln., after extracting Fe with *iso*propyl ether. *Procedure*—The sample of metal (1 g) is dissolved in an oxidising acid mixture, and the soln. is evaporated to dryness. The residue is dissolved in 20 ml of H_2O and 40 ml of HCl (sp. gr. 1·19) and transferred to a separating funnel with 20 ml of H_2O and 10 ml of HCl. Two extractions with *iso*propyl ether (60 ml and then 30 ml) remove the Fe. After evaporating the aq. layer to a small vol., 5 ml of HNO_3 (sp. gr. 1·33) and 10 ml of H_2SO_4 (1:1) are added and the soln. is heated to fuming. The residue is dissolved in 5 ml of HCl and 20 ml of H_2O, and the soln. is made up to 500 ml. One ml of Na acetate soln. (50 per cent. w/v), 5 ml of the metal soln., 15 ml of H_2O and 50 ml of 2-nitroso-1-naphthol soln. are introduced into a 100-ml Erlenmeyer flask, and after being warmed for 5 min. at 85° to 90° C, the soln. is allowed to stand overnight. The liquid is transferred with 10 ml of H_2O to a separating funnel and shaken for 2 min. with 25 ml of toluene (measured exactly). The organic layer is separated and washed successively with 20 ml of an aq. acid soln. (30 g of citric acid and 50 g of acetic acid made up to 500 ml), 20 ml of acetic acid soln. (10 per cent.) and three times with 20 ml of 2 *N* NaOH. The toluene soln. is set aside for an hour or two, then carefully decanted and allowed to stand for a further 2 hr. The extinction is measured in a 3-cm cell at 530 mμ relative to pure toluene. The 2-nitroso-1-naphthol reagent, which is stable for a week, is prepared from 300 ml of Na citrate soln. (250 g of trisodium citrate and 25 ml of 10 *N* NaOH made up to 500 ml), 50 ml of glacial acetic acid, 10 ml of a filtered 1 per cent. soln. of 2-nitroso-1-naphthol in acetic acid and 100 ml of

H_2O. The soln. is warmed to between 85° and 90° C, allowed to cool for a few hours, filtered and made up to 500 ml. J. H. WATON

2100. **Detection of cobalt and nickel in a single sample by dissolution of their sulphides.** M. P. Babkin. *Soobshch. Nauch. Rabotakh Chlenov Vsesoyuz Khim. Obshchestva*, 1954, (2), 46–47; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,468.—Various vol. of 0·1 *N* $NiSO_4$ and $Co(NO_3)_2$ in centrifuge tubes were mixed with $(NH_4)_2S$ soln., the ppt. were centrifuged and washed with water. The washed ppt. were treated with 2 to 3 ml of 20 per cent. KNO_2 soln. and 1 to 2 ml of 2 *N* acetic acid, and heated to decompose the black ppt. Cobalt gave a yellow cryst. ppt. Nickel was detected in the soln. by means of dimethylglyoxime. With a Co to Ni ratio of 1:4, 0·4 mg of Co can be detected, and with a Co to Ni ratio of 50:1, 0·04 mg of Ni can be detected. G. S. SMITH

2101. **Co-precipitation of cobalt with nickel dimethylglyoxime.** G. K. Schweitzer and B. L. McDowell (Univ. of Tennessee, Knoxville, Tenn., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (2), 115–120.—The co-precipitation of Co^{++} with Ni^{++} by dimethylglyoxime has been investigated under various conditions and with the use of Co labelled with ^{60}Co to facilitate its determination. Pptn. were carried out in ammoniacal soln., in acetate soln. at 25° and 85° C, with slow and rapid addition of the pptg. agent, and with various digestion times. Minimum co-precipitation (1·3 to 3·9 μg of Co) was achieved by slow addition of aq. NH_3 to the acid soln. of Ni^{++} (57·6 mg), Co (612 μg) and dimethylglyoxime, followed by a digestion period of 30 min. The temp. throughout was 25° C.
W. C. JOHNSON

2102. **Conductimetric titration of certain salts with barium hydroxide. I. Titration of nickel sulphate.** M. I. Usanovich, Z. P. Yakusheva and S. V. Lebedeva. *Uch. Zap. Kazakh. Univ.*, 1954, **16**, 21–26; *Ref. Zhur., Khim.*, 1955, Abstr. No. 23,981.—Conductimetric titration with $Ba(OH)_2$ solution can be used for the titration of solutions of $NiSO_4$, $NiSO_4$ and H_2SO_4, and $NiSO_4$ in the presence of Na_2SO_4 and of Na_2SO_4 and H_2SO_4, but the presence of KCl decreases the accuracy of the determination of $NiSO_4$, and Na_2SO_4 cannot be titrated in the presence of $NiSO_4$. G. S. SMITH

2103. **Volumetric determination of nickel and palladium by the method of flotation titration with dimethylglyoxime.** A. G. Karabash. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 279–293; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,469.—Titrations are carried out in a separating funnel containing the liquid to be titrated and a heavy immiscible solvent. Periodically the solvent to which the ppt. formed in the reaction has been attracted is run off and fresh solvent is introduced. Nickel is titrated with dimethylglyoxime solution in weakly ammoniacal medium with CCl_4 as the immiscible solvent, and Pd is titrated similarly in 0·1 to 0·2 *N* HCl or H_2SO_4 with $CHCl_3$ as the immiscible solvent. In steel, Ni can be determined in this way after separation of Fe by Tananaev's fluoride method. The methods for Ni and Pd are as accurate and reproducible as the corresponding gravimetric methods. G. S. SMITH

2104. **Spectrochemical analysis of refined rhodium.** C. L. Lewis, W. L. Ott and J. E. Hawley (Falconbridge Nickel Mines, Richvale, Ont., Canada). *Canad. Mining Met. Bull.*, 1955, **516**, 208–212.—Spectrographic methods for determining minor constituents in rhodium sponge are far superior to wet chemical methods. The "sponge" technique is most suitable for determining Ir, Pd, Fe, Ni and Cu, and a modified sponge technique is used for SiO_2. Other elements are determined by the "black" technique. Solutions can be analysed by coated-electrode or porous-cup techniques. "Sponge" (metal powder) and "black" (very finely divided metal powder) are most easily handled as briquets or pellets. Directions are given for the preparation of pellets from the sample and standards. A high-voltage spark discharge from a High Precision Source unit is used for excitation. CHEM. ABSTR.

2105. **Detection of palladium with lauryl mercaptan [*n*-dodecanethiol].** M. Ziegler and O. Glemser (Inorg. Chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1956, **146** (1–2), 101–103.—*Procedure*—Mix the weakly acidic (HCl) sample solution (1 ml) with 2 per cent. *n*-dodecanethiol in methanol (3 to 5 drops) and extract with amyl alcohol (5 drops). A yellow film at the interface or a yellow colour in the alcohol indicates the presence of Pd. The method is sensitive down to 0·3 μg of Pd at a concn. of 1 in 3×10^6. Only Pb interferes seriously (yellow colour with reagent) and must first be separated as $PbSO_4$; this reduces the sensitivity to 3 μg of Pd. Differentiation between Pb and Pd is possible by dissolution of the ppt. in heptanol - *n*-dodecanol (2:5 by vol.), when Pd gives a yellow and Pb a colourless solution. A white ppt. is given by Hg^{II} (removed by heating) and Au gives a weak reddish colour in the amyl alcohol phase. J. P. STERN

2106. **(Ethylenedinitrilo)tetra-acetic acid [EDTA] chelation of platinum group metals. Spectrophotometric determination of iridium.** W. M. MacNevin and O. H. Kriege (Ohio State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (1), 16–18.—The use of EDTA (disodium salt) (**I**) has enabled the effective concn. range for the spectrophotometric determination of Ir to be extended down to 2·5 p.p.m. Beer's law is obeyed over the range 3 to 75 p.p.m. at a pH range of 11·5 to 12·6. The reagent **I** is added in two to three-fold excess; the full colour is developed at 80° to 90° C within 10 min., and remains stable for at least 12 hr. The colour is unaffected by SO_4'', but NO_3' should be absent. The wavelength of max. absorption was found to be 313 mμ and the measurement was made in 10-mm silica cells at controlled sensitivity. Potassium hydroxide was employed for the initial pH adjustment. The effect of other metals of the platinum group was studied and, for an error of ± 2 per cent. in the detection of 1·00 mg of Ir, the following quantities (in mg) are permissible: Pd^{++} (0·1), Pt^{++} (0·7), Pt^{++++} (0·2), Rh^{+++} (0·07), Os^{++++} (0·06) and Ru^{+++} (0·02); when larger amounts of interfering metals are present a preliminary separation of Ir is recommended. D. G. HIGGS

See also Abstracts 1960, 1961, 1963, 1966, 1969, 1970, 2318, 2361, 2362.

3.—ORGANIC ANALYSIS

2107. **Technique of determining radio-carbon in organic compounds.** V. G. Vasil'ev (L. Ya. Karpov Phys. Chem. Inst., Moscow). *Zhur. Anal. Khim.*, 1955, **10** (6), 368–372.—The organic compound containing ^{14}C is burnt in O and the CO_2 is converted into $BaCO_3$, which is formed into a disc in a special apparatus. The activity is measured by means of a Geiger counter. A formula for calculating the absolute radioactivity of $BaCO_3$ samples from comparisons with uranium standards is given.
G. S. SMITH

2108. **Isotope dilution - static combination method for organic carbon in submilligram specimens.** R. N. Boos, S. L. Jones and N. R. Trenner (Merck & Co. Inc., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 390–392.—The method is based on the static combustion of a weighed mixture of the unknown material and a known ^{13}C-labelled tracer compound. The combustion is performed in evacuated sealed ampoules, which are broken, after combustion is complete, within the evacuated inlet system of the mass spectrometer, and the $^{13}CO_2$ to $^{12}CO_2$ ratio is measured. Copper oxide is used as the oxidising agent within the ampoule. An accuracy within $\pm$ 1 per cent. is achieved with samples as small as 200 μg, provided a micro-balance is used.
G. P. COOK

2109. **Ampoule combustion - isotope-dilution technique for organic nitrogen.** S. L. Jones and N. R. Trenner (Merck & Co. Inc., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 387–390.—The sample, consisting of the tracer or tracer and unknown, is sealed with an excess of CuO in an evacuated ampoule and heated in a furnace to complete combustion. The ampoule is opened in a special evacuated apparatus and the combustion gases after absorption of CO_2 and water are passed into a mass spectrometer, where the isotope ratio of the N is determined. The precision is limited chiefly by the weighing error, which may be as large as $\pm$ 2·0 per cent.
G. P. COOK

2110. **Double combustion method for quantitative determination of sulphur in organic compounds.** N. P. Volȳnskiĭ and I. K. Chudakova (Inst. of Petroleum, Acad. Sci., U.S.S.R.). *Zavod. Lab.*, 1955, **21** (12), 1435–1439.—In the double combustion method the vapour of the substance being analysed or the products of its pyrolysis are introduced into the flame of a sulphur-free solvent, *e.g.*, dioxan, and the oxides of S are absorbed in a solution of NaOH or Na_2CO_3. Apparatus for the purpose is described. The method is applicable to organic substances containing C, H, O, N and S.
G. S. SMITH

2111. **Mercurimetric method of determining halides in organic compounds.** L. N. Lapin and R. Kh. Zamanov (I. P. Pavlov Samarkand Med. Inst.). *Zhur. Anal. Khim.*, 1955, **10** (6), 364–367.—The organic compound is decomposed by Na and a 15 per cent. soln. of ethanediol in *iso*butyl alcohol (modified Stepanov method), and the halide is determined by titration with 0·05 *N* $Hg(NO_3)_2$ in the presence of diphenylcarbazone as indicator.
G. S. SMITH

2112. **Determination of fluorine in organic compounds.** M. O. Korshun, V. A. Klimova and M. N. Chumachenko (Inst. Elem. Org. Comp., Acad. Sci., SSSR, Moscow). *Zhur. Anal. Khim.*, 1955, **10** (6), 358–363.—The fluorine compound is decomposed by heating with K in a steel bomb at 800° to 850° C for 10 to 15 min. The fluoride obtained is titrated with 0·025 *N* $Th(NO_3)_4$. Halides, N and S do not interfere. Phosphorus interferes but can be allowed for; the total of F and P is determined in one aliquot, and P alone is determined in another aliquot after removal of F by repeated evaporation with conc. HCl.
G. S. SMITH

2113. **Determination of fluorine in organic compounds.** A. Ya. Savchenko (K. E. Voroshilov Sci. Res. Inst. of Org. Intermediates and Dyestuffs, Moscow). *Zhur. Anal. Khim.*, 1955, **10** (6), 355–357.—Decomposition of fluorine-containing substances by heating with Na in a nickel bomb at 650° to 700° C as described by Belcher and Tatlow (*Analyst*, 1951, **76**, 593) gave low and variable results. Decomposition at 900° to 950° C for 2 hr. with K is recommended. The sample containing 20 to 25 mg of F is heated with 2 to 3 times its wt. of K. The contents of the bomb are carefully treated with water and the soln. is made up to 140 to 150 ml. After neutralisation with 10 per cent. HCl soln. to a pale pink, with sodium alizarinsulphonate (2 drops of 0·5 per cent. soln.) as indicator, the soln. is heated on a boiling-water bath for 1 to 1·5 hr., cooled and diluted to 150 ml. Four drops of the indicator and sufficient 10 per cent. HCl soln. to give a bright yellow colour are added and the soln. is titrated with zirconium chloride soln. until the colour becomes brown - yellow. If S is present the heating of the neutralised soln. is followed by filtration. The method is satisfactory in the presence of Cl, N and S.
G. S. SMITH

2114. **Determination of fluorine in organic compounds by a combustion method.** Rimpei Kojima, Shunji Nagase and Hiroshige Muramatsu (Gov. Ind. Res. Inst. of Nagoya, Hirate-machi, Kita-ku, Nagoya). *Japan Analyst*, 1955, **4** (8), 518–521.—The combustion tube (made of silica) for organic compounds containing F was modified so that it could be used for gas, liquid or solid samples. Solids and liquids are volatilised and passed into the combustion tube with a stream of oxygen containing NH_3 (rate of flow, 25 ml per min.). The silica tube is heated at 1000° C and the product, containing HF, is absorbed in water, which is neutralised and titrated with $AlCl_3$ soln., with Eriochrome cyanine as indicator. The amount of total F treated in this apparatus must be < 20 mg.
K. SAITO

2115. **Electrometric titration of compounds containing positive chlorine or bromine with sulphur dioxide in pyridine.** R. W. Freedman (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 247–249.—By utilising the Karl Fischer reaction, it is possible to titrate I or Br liberated quant. (*e.g.*, from N-halogeno compounds by addition of KI or KBr) with SO_2 in pyridine - methanol soln. containing not less than a twofold excess of water. Very sharp end-points are obtained visually or electrometrically; the precision is $\simeq$ 0·12 per cent. and the accuracy is within 0·4 to 0·8 per cent. The standard SO_2 soln. can vary in concn. from 5 *N* to 0·5 *N*, is reasonably stable and can be standardised by iodimetric titration with $K_2Cr_2O_7$ by using an electrometric end-point, namely, 0 to 5 μA at 200 mV. A suitable titration apparatus is shown.
W. J. BAKER

2116. **Rapid gravimetric determination of mercury in organic compounds.** H. F. Walton and H. A. Smith (Univ. Colorado, Boulder, Colo., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 406–407.—The compound is decomposed by refluxing with HI containing I; Hg forms HgI_4'', which are pptd. and weighed as the cupric propylenediamine mercuri-iodide. Compounds such as methylmercury hydroxide, bromide and iodide and diphenylmercury give precise results, but with an accuracy of $\simeq -1{\cdot}0$ per cent. Part of this error is caused by incomplete pptn. G. P. Cook

2117. **Quantitative analysis by the use of infra-red spectra. IV. The limit of determination of impurities in raw materials for organic synthesis.** Hitoshi Kamada, Shigeyuki Tanaka and Shoji Hayashibara (Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1955, **4** (9), 545–546.—The limit of determination of impurities (toluene, thiophen, benzene, toluidines, cresols, etc.) in organic substances such as benzene, aniline, nitrobenzene and cresols was studied by the use of the Baird i.r. spectrograph, with reference to the concn. of the reference soln. inserted in the compensating optical path. When the concn. is too high, the total amount of the transmitted i.r. rays is too small to be accurately measured. The concn. should be so adjusted that the transmission at the key band becomes 30 to 40 per cent. For most of the above-mentioned examples, the minimum concn. of impurities that can be accurately determined is $\simeq 0{\cdot}1$ per cent. K. Saito

2118. **4-Phenylthiosemicarbazide as reagent for the characterisation of aldehydes and ketones.** M. Tišler (Inst. Org. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1956, **149** (3), 164–172.—4-Phenylthiosemicarbazide (**I**) is a useful reagent for characterisation of carbonyl compounds. Many of the 4-phenylthiosemicarbazones, particularly those of aromatic aldehydes, are high melting and have sharp m.p. Lower aliphatic aldehydes (such as acet-, propion-, *n*-butyr-, *iso*-valer-, and croton-aldehyde) give non-cryst. 4-phenylthiosemicarbazones, and anthraquinone, *o*-benzoylbenzoic acid, Michler's ketone, and camphor also behave anomalously. Melting points and infra-red spectra between 2 and 15 μ (which serve to distinguish derivatives of similar m.p.) of a large number of these derivatives are given. *Preparation of derivatives*—To 0·0025 mole of carbonyl compound in 96 per cent. alcohol (7 to 10 ml) add 0·0025 mole of **I** and heat under reflux for 30 min. Cool, filter off (or concentrate and filter off), and recrystallise from alcohol. J. P. Stern

2119. **Chromatographic separation of alcohols as xanthates.** J. W. Spanyer and J. P. Phillips (Univ. Louisville, Louisville, Ky., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 253.—Satisfactory separation of C_1 to C_5 alcohols can be achieved by chromatography of their xanthates on a cellulose column. Recoveries of > 95 per cent. of the xanthates were obtained from 17 out of 21 alcohol pairs selected for separation. Identification of the xanthates was made by conversion into insol. thallous salts having characteristic melting points. G. P. Cook

2120. **Thermometric determination of water and acetic anhydride in acetic acid.** L. H. Greathouse, H. J. Janssen and C. H. Haydel (S. Regional Res. Lab., New Orleans, La., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 357–361.—The methods described are based on the exothermic reaction of water and acetic anhydride in glacial acetic acid soln. The reaction is catalysed by a trace of $HClO_4$. In the first method the temp. rise is measured by basic calorimetry, and in the second either the water or the anhydride is titrated in glacial acetic acid soln. with the other, until no further temp. rise occurs. Good agreement between the two techniques was reached and the determination of water agreed closely with the Karl Fischer method. Accuracy and reproducibility were generally within ± 2 per cent. for all the techniques. G. P. Cook

2121. **Oxidation of oxalic acid in glacial acetic acid with cerium (IV).** O. N. Hinsvark and K. G. Stone (Mich. State Univ., East Lansing, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 334–337.—The oxidation of oxalic acid in glacial acetic acid requires two equivalents of Ce^{IV} and this reaction may be used to determine oxalic acid provided that the soln. is made *N* in $HClO_4$, which speeds up the reaction to a reasonable rate. A soln. of ammonium hexanitratocerate in glacial acetic acid can be used as the titrant. The accuracy is generally within $\pm 0{\cdot}5$ per cent. in the presence of a number of oxygenated compounds. G. P. Cook

2122. **The separation and determination of micro quantities of lower aliphatic acids, including fluoroacetic acid.** F. Bergmann and R. Segal (Hebrew Univ. Hadassah Med. Sch., Jerusalem, Israel). *Biochem. J.*, 1956, **62** (4), 542–546.—Fluoroacetic acid is separated from formic and acetic acids and other straight-chain fatty acids by paper chromatography of the hydroxamates with aq. NH_3 - ethanol - dil. pyridine. The hydroxamic acids are determined by direct oxidation with iodine to HNO_2, which is used to diazotise sulphanilic acid. The resulting diazo compound is determined by coupling with 1-naphthylamine. The method, which involves two-dimensional paper chromatography of the hydroxamic acids, extraction, and formation of the dye, has a lower limit of 0·5 μg per ml of final solution. J. N. Ashley

2123. **Chromatographic separation and determination of straight-chain saturated monocarboxylic acids C_1 through C_{10} and dicarboxylic acids C_{11} through C_{16}.** G. B. Corcoran (Armour and Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 168–171.—A series of three columns with stationary phases at different pH values is employed for the determination of C_1 to C_{10} monocarboxylic acids and a series of two columns at different pH values is used for the determination of C_{11} to C_{16} dicarboxylic acids. The stationary phase is 2 *M* aq. glycine on silicic acid adjusted to the required pH and the mobile phase is *n*-butanol - chloroform. The accuracy is within $\pm 1{\cdot}0$ per cent. for all components. G. P. Cook

2124. **Permanganometric determination of certain organic hydroxy acids.** V. K. Zolotukhin and A. S. Molotkova. *Trudy Komissii Anal. Khim. Akad. Nauk, SSSR*, 1954, **5** (8), 179–185; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,519.—Calcium and copper salts greatly accelerate the oxidation of tartrate with permanganate in alkaline medium and permit a quant. determination of tartrate. Oxidation of citrates is incomplete and Ca, Fe and Cu show no accelerating action. There is scarcely any difference between the amount of citrate oxidised

(≃ 79·2 per cent.) by permanganate in 1·5 hr. and 24 hr. Thus an empirical factor can be used in determining citrates. Salicylic acid is almost completely oxidised (99·45 per cent.) by permanganate in alkaline medium in 3 hr.; the longer time recommended in the literature is not necessary.
G. S. SMITH

2125. **Colorimetric method for determination of sugars and related substances.** M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers and F. Smith (Univ. Minn., St. Paul, Minn., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 350–356.—The method is based on the colour obtained by the reaction of simple sugars, oligosaccharides, polysaccharides, and their derivatives with phenol in the presence of conc. H_2SO_4. Absorption data for 30 carbohydrates are listed and under the conditions described the accuracy is within ± 2 per cent. When used in conjunction with partition paper chromatography, an accuracy within ± 5 per cent. is attained.
G. P. COOK

2126. **Applications of nitrometry. V. Determination of reducing sugars.** Masaharu Yamagishi and Makoto Yokoo (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (9), 958–960.—Aldoses (hexoses as well as pentoses) and ketoses are oxidised with $K_3Fe(CN)_6$ in a phosphate buffer (pH 11 to 12). The excess of $K_3Fe(CN)_6$ is treated with a basic soln. of hydrazine hydrate (**I**) and the resulting nitrogen is determined with a nitrometer. The sample (10 to 120 μg in 1 to 2 ml of water) is heated with phosphate buffer (1 ml) and $K_3Fe(CN)_6$ (0·2 per cent., 1 ml) on a water bath for 30 min. The product is introduced into a nitrometer confined with a saturated soln. of NaCl, and submitted to nitrometry, with the use of **I** soln. (10 ml of 40 per cent. NaOH are mixed with 0·5 ml of 60 per cent. **I**). The standardisation of the $K_3Fe(CN)_6$ soln. is carried out similarly. The ratio of the initial amount of $K_3Fe(CN)_6$ (expressed in ml of N) to that consumed by the reduction of a unit amount of saccharide is constant for aldohexoses, aldopentoses and ketohexoses. Non-reducing saccharides, including sucrose, trehalose and cellulose, fail to reduce $K_3Fe(CN)_6$ under the given conditions.
K. SAITO

2127. **Determination of specific activity of carbon-14-labelled sugars on paper chromatograms using an automatic scanning device.** H. R. Roberts and F. J. Carleton (Nat. Dairy Res. Lab., Inc., Oakdale, L.I., N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 11–16.—Results are reported on the chromatographic separation of "labelled" sugars in which paper strips and elution with ethyl acetate - pyridine - H_2O (2·5 : 1 : 3·5) were used. The three sugars studied were [1-^{14}C]lactose, [1-^{14}C]galactose and [1-^{14}C]glucose. The developed strip was subjected to automatic scanning by a device which records the activity of the separated bands. Two methods of quant. determination of specific activity are reported: (*i*) employs summation equations involving the areas under the curves and the total specific activity of the soln. being analysed, and (*ii*) employs comparison of the heights of unknown soln. with a calibration curve prepared from the measured heights of known ^{14}C-labelled sugar soln. The determination of the specific activity of ^{14}C-labelled sugars by either method was within ± 3 per cent. of the true value.
D. G. HIGGS

2128. **Temperature effects in the paper partition chromatography of sugars.** M. Alcock and J. S. Cannell (Thos. Kerfoot & Co. Ltd., Ashton-under-Lyne, Lancs., England). *Nature*, 1956, **177**, 327–328.—The small all-metal apparatus for controlled-temp. chromatography previously described (*Anal. Abstr.*, 1954, **1**, 2567) has been used for studying the R_F values of a number of sugars throughout the temp. range 0° to 50° C. Separations were carried out on strips of Whatman No. 1 paper 6 in. wide and cut across the machine direction of the paper. Fifteen sugars were compared on each paper by preparing five solutions, each containing three different sugars, and after application of the spots the apparatus was set aside for ≮ 4 hr. for equilibrium to be established. Only two-component solvent systems were studied. The results showed that R_F values vary considerably with temp. and that the factor exerting the greatest influence is the water content of the solvent. Changes in temp. also influence the speed of development of the chromatogram, since physical characteristics of the solvent, and hence the "diffusion coeff." of the paper, are affected.
K. A. PROCTOR

2129. **Separation of three mono-O-methyl-D-glucoses.** R. W. Lenz and C. V. Holmberg (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 7–8.—The three possible mono-O-methyl-D-glucose isomers, 2-O-, 3-O- and 6-O-methyl-D-glucoses, have been successfully separated by paper-strip chromatography. Elution by downward displacement with 2 : 4 : 6-collidine - ethyl acetate - H_2O (2 : 5 : 5) over a period of 65 hr. was found to be effective provided that the paper strip was removed every 15 hr. and dried (to sharpen the spots). The sugar spots were located by spraying with *p*-anisidine hydrochloride (3 per cent.) in *n*-butanol, followed by heating at 100° C for 10 min. Quantitative determination was made by the method of Hirst *et al.* (*J. Chem. Soc.*, 1949, 928). After treatment with *p*-anisidine hydrochloride, the spots for the 2-O-, 3-O- and 6-O-isomers were lavender, yellowish brown and brownish yellow, respectively.
D. G. HIGGS

2130. **Spectrophotometric method for quantitative evaluation of early stages of hydrolyses of branched components of starches by α-amylases.** J. W. Van Dyk and M. L. Caldwell (Columbia Univ., New York, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 318–320.—The method is an adaptation of that of McCready and Hassid (*J. Amer. Chem. Soc.*, 1943, **65**, 1154) in which spectrophotometric measurements were made on the iodine complexes with substrates and certain of their hydrolysis products, from the amylase hydrolysis of linear components of starches. This technique was successfully adapted for the study of the early stages of hydrolysis of fat-free waxy maize starch by crystalline pancreatic amylase. The standard deviation of the method is ± 0·09 per cent. of theoretical glucose or ± $3·5 \times 10^{-7}$ mole of aldehyde groups per litre and the limiting concn. is 0·00625 per cent. of waxy maize starch. The method is applicable to the study of the hydrolysis of branched components of other starches by pancreatic or other α-amylases.
G. P. COOK

2131. **Colorimetric determination of aliphatic α-nitrohydroxy compounds.** L. R. Jones and J. A. Riddick (Commercial Solvent Corp., Terre Haute, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 254–255.—

The method is based on the decomposition of nitro alcohols to formaldehyde and a nitroparaffin in the presence of excess of alkali. The formaldehyde is determined, colorimetrically, as the chromotropic acid complex. Amino alcohols do not react and 1000 p.p.m. of nitro alcohol in amino-alcohol samples can be determined. The accuracy is within ± 2·0 per cent. and the precision within ± 1·0 per cent. over the concentration range of 1 to 100 μg of nitro alcohol. G. P. Cook

2132. **The rapid determination of urea by oxidimetric titration.** J. Bitskei (Polytech. Univ. Budapest). *Magyar Kém. Foly.*, 1956, **62** (2), 71–72.—Urea is rapidly oxidised by NaOCl in weakly alkaline solution, in the presence of Br′, but the Br′ also use up some NaOCl slowly. *Procedure*—To the urea-containing soln., add H_3BO_3 (2·5 to 3 g), KBr (0·1 to 0·2 g) and water (10 to 20 ml) and warm to between 50° and 60° C. To the warm and stirred soln. add an excess of 0·1 *N* NaOCl (which should contain *N* NaOH) from a burette. Warm the flask on the water bath and shake it occasionally. After 2 min., add 30 per cent. NaOH (10 ml) and an accurately measured vol. of 0·1 *N* $Na_2S_2O_3$, equivalent to the NaOCl added. Cool the soln., add 1 per cent. ethanolic brazilin and 5 per cent. KI (1 drop of each) and titrate slowly with 0·1 *N* NaOCl. The colour change is from red to green. The accuracy is within ± 2 per cent. A. G. Peto

2133. **Determination of water in 1:1-dimethylhydrazine and hydrazine by a high-frequency method.** R. D. Weaver, G. C. Whitnack and E. St. Clair Gantz (U.S. Naval Ord. Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 329–332.—The water - 1:1-dimethylhydrazine and water - hydrazine systems were studied with an oscillometer, and the data obtained for the two systems are presented graphically over the range 0 to 100 per cent. of water. Mean values of 100·4 and 98·9 per cent. were obtained at 2 and 0·7 per cent. levels, respectively, of water in 1:1-dimethylhydrazine, with a standard deviation of ± 1·7 per cent.; the variation of results, for 0 to 10 per cent. of water in hydrazine, was too large for analytical application. G. P. Cook

2134. **Determination of small amounts of xanthate in aqueous solutions by potentiometric titration.** I. N. Plaksin, N. A. Suvorovskaya and A. M. Okolovich (Inst. Mining, Acad. Sci., USSR). *Zavod. Lab.*, 1956, **22** (1), 28–30.—The xanthate solution (100 to 150 ml) is titrated potentiometrically with 0·00025 to 0·001 *N* $AgNO_3$. The working electrode is a silver wire and the reference electrode the S.C.E. The titrant is standardised on pure potassium butylxanthate. G. S. Smith

2135. **Determination of organic thiocyanates by use of the reaction with alkali polysulphides. I. The reaction between benzyl thiocyanate and various alkali sulphides.** Kiyoshi Takiura and Yoshio Takino (Pharm. Inst., Medical Faculty, Osaka Univ., Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (8), 839–842.—Reactions of NaHS, Na_2S, Na_2S_2, Na_2S_3, Na_2S_4 and Na_2S_5 with benzyl thiocyanate (**I**) were studied in ethanolic soln. of different water content. Aqueous Na_2S_3 soln. (≃ 10 per cent.) reacts with **I** in 10 per cent. ethanolic soln. (100 ml) on a boiling-water bath, within 10 min., to produce SCN′, equiv. in amount to **I** (50 to 200 mg), and dibenzyl disulphide. The soln. is treated with dil. H_2SO_4 (2·5 ml) to give a pH of 1·8 to 2·0 then heated on a water bath (90 min.) to remove the excess of H_2S. The clear liquid is titrated with $AgNO_3$ soln., with iron alum as indicator. The amount of Na_2S_3 must be > 5 times the equiv. of **I**. The error is about ± 0·2 per cent. The use of Na_2S does not provide good results, presumably because of the interaction of OH′ with **I** to give CN′ and OCN′.

II. Reaction of various organic thiocyanates with sodium trisulphide. Kiyoshi Takiura, Yoshio Takino and Osamu Kondo. *Ibid.*, 1954, **74** (8), 843–845.—The reaction described above was examined with various aliphatic and aromatic thiocyanates. Satisfactory results were obtained by a similar titration, with the same error as for **I**. Thiocyanate ions thus produced can also be detected with $FeCl_3$ on a micro scale (limit of detection, 1 μg; limit of concn., 1 in 10,000). Any *iso*thiocyanate resulting from the isomerisation of thiocyanate on heating does not cause any significant error. Some aliphatic nitriles produce SCN′ on interaction with alkali polysulphides, but the amount is negligible. K. Saito

2136. **Determination of benzene, toluene and xylene in mixtures.** L. Grzelewski and S. Ciborowski. *Przem. Chem.*, 1955, **11**, 375–380.—A cheap and rapid quantitative method of determining benzene (excess) in admixture with toluene (**I**) and xylene (**II**) (0 to 18 per cent.) is described. It is accurate to within 0·4 per cent. and consists of a single standard distillation of 100 ml of the mixture, the temperatures at which 20 ml and 80 ml of distillate are collected being noted. These temperatures are functions of (**I** + **II**) and **I**/**II**, respectively. The relative proportions of the hydrocarbons are read from graphs obtained by standard distillations of mixtures of known composition. A number of these graphs and tables are given. A. O. Jakubovic

2137. **The simultaneous determination of traces of benzene and toluene.** W. Hancock and E. Q. Laws (Gov. Lab., Clement's Inn Passage, Strand, London). *Analyst*, 1956, **81**, 37–41.—In this method conditions of nitration of benzene and toluene are so chosen that the products are *m*-dinitrobenzene and 2:4:6-trinitrotoluene. The benzene and toluene, or their nitration products, are collected in nitration acid (HNO_3 and H_2SO_4, 1:20 v/v) and the liquid is heated at 105° C for 2 hr. The diluted liquid is extracted with ether and the extracted nitration products are transferred into solution in alkaline purified butanone. Extinction measurements are made at 462 and 565 mμ. Standard soln. of *m*-dinitrobenzene and 2:4-dinitrotoluene are treated in the same way, and from the standardisation data the constants in a pair of simultaneous equations are obtained. Solution of these equations provides the amounts of *m*-dinitrobenzene and 2:4:6-trinitrotoluene in the sample soln. The method is empirical and the constants in the equations may vary with different batches of butanone; but with identical treatment of sample and standards, losses due to parallel nitration reactions and oxidation are constant proportions of the amounts present. The *m*-dinitrobenzene figure tends to be low and the 2:4:6-trinitrotoluene figure high. The method is applicable in the range 0 to 50 μg of both nitration products. A. O. Jones

2138. **New iodimetric procedure for the determination of phenol in the presence of reducing substances.** E. Schulek and K. Burger (Inst. Inorg. and Anal. Chem., Eötvös Loránd Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1955, **61** (11), 359–362.—When phenol is brominated with an excess of bromine, four bromine atoms become attached to the molecule. Of these, that attached to the oxygen can be determined iodimetrically. *Procedure*—Dilute the soln. containing 2 to 10 mg of phenol to between 30 and 50 ml with water, in a ground-glass stoppered flask. Add saturated bromine water until the liquid (which contains a ppt.) is reddish brown. After 20 min., add 20 per cent. Na_2SO_3 soln. till the colour becomes yellow, followed at once by 5 per cent. phenol soln. (5 ml) to remove any remaining bromine. Shake the soln. and add immediately KI (0·5 g) and 20 per cent. HCl (5 ml). After 10 to 15 min., add a few drops of starch soln. and titrate the iodine with 0·01 *N* $Na_2S_2O_3$. The accuracy is $\pm$0·5 per cent. Small (2 to 5 mg) amounts of phenol can be determined accurately in the presence of a large excess of sulphite (0·2 g) and sulphide (0·1 g).

A. G. Peto

2139. **Non-aqueous titration of phenols. I. A new indicator, 4-amino-4′-nitroazobenzene.** Kiyoshi Takiura and Yoshio Takino (Osaka Univ., Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (9), 971–972.—In acidic soln. in ethylenediamine or in pyridine, 4-amino- 4′-nitroazobenzene shows a red coloration, which changes to blue on the addition of K methoxide. The change in colour is so marked that it can be applied to the titration of monobasic phenols, carboxylic acids and amino acids. Hydroxycarboxylic acids, such as salicylic or *p*-hydroxybenzoic, behave in ethylenediamine as dibasic acids. Substituted phenols, including nitrophenol, hydroxybenzaldehydes and hydroxyacetophenones can also be titrated in pyridine, with *p*-nitrophenylazoresorcinol as indicator.

K. Saito

2140. **Periodate test for the catechol and hydroquinone [quinol] structures.** O. C. Windrath (Niagara Univ., Niagara, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 263.—Treatment of methanolic soln. of organic compounds containing a catechol or quinol grouping with aq. sodium metaperiodate results in the formation of a crystalline ppt. within 0·5 hr.

G. P. Cook

2141. **Spot test for diketones and quinones based on catalytic effect.** F. Feigl and C. Costa Neto (Min. Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1956, **28** (3), 397–399.—The slow reaction between formaldehyde and 1:2-dinitrobenzene, which yields a violet alkali salt of the aci-form of *o*-nitronitrosobenzene, is hastened by the additions of 1:2-diketones and quinones. This reaction is the basis for the identification of these types of compounds, 12 of which gave successful results. New micro tests are made possible for anthracene, phenanthrene and inositol by their ready conversion into quinones or polyketones.

G. P. Cook

2142. **Quantitative determination of 2:4-dinitro-o-cresol, 6-sec.-butyl-2:4-dinitrobutylphenol and 2:4-dinitro-o-*iso*propylphenol.** H. Zeumer (Biol. Bundesanstalt für Land- und Forstwirtschaft, Brunswick, Germany). *Z. anal. Chem.*, 1956, **148** (6), 403–412.—These active agents in plant insecticides can be determined colorimetrically by using the orange soln. produced when each of the dinitro compounds is reduced with glucose in the presence of NaOH and ethanol (Bose reaction). *Procedure*—If the preparation is not oily, enough to contain $\simeq$ 0·25 g of dinitro compound is dissolved in 10 per cent. NaOH soln. and the vol. is made up to 250 ml. A 25-ml aliquot is made up to 100 ml with 10 per cent. NaOH soln. Aliquots of this soln. (1, 3 and 5 ml) are introduced into test-tubes, and enough 10 per cent. NaOH soln. is added to make a vol. of $\simeq$ 10 ml. Then 5 ml of 96 per cent. ethanol and 1 ml of 1 per cent. aq. glucose soln. are added, and the tubes are well shaken and kept at a temp. of 60° C in a water bath for 20 min. A blank is prepared from 10 ml of 10 per cent. NaOH soln., 5 ml of alcohol and 1 ml of glucose soln. After being cooled, the soln. are transferred in turn to a 100-ml stoppered cylinder, and made up to 100 ml. The soln. is well shaken, and the extinction is then measured with an S45E filter in 1-cm cells against that of the blank. If the preparation is oily, this procedure is followed as far as the production of 100 ml of an emulsion. The emulsion is centrifuged at 3500 r.p.m. for 45 min., and then 1-, 3- and 5-ml aliquots of the aq. layer are used for the determination, completed as described above. Standardisation curves are plotted for each of the dinitro compounds. The results show an error of $\simeq \pm$ 1·5 per cent., although in the presence of tar oils this rises to $\simeq \pm$ 3 per cent.

J. H. Waton

2143. **Colour reactions of nitroindanedione. I. Reactions with phenols, alkaloids and pyrroles.** G. Vanag and M. Matskanova. *Izv. Akad. Nauk Latv. SSR.*, 1954, (10), 143–146; *Ref. Zhur., Khim.*, 1955, Abstr. No. 24,040.—Nitroindanedione gives orange or red colorations with resorcinol, trihydric phenols, certain alkaloids and pyrroles. The reactions with alkaloids are of low sensitivity and not specific, but resorcinol can be differentiated from orcinol, and the red colorations with pyrroles, which occur at room temp. in aq., alcoholic and acetic acid solutions, are very characteristic and sensitive. For the colorations with phenols and alkaloids heating is required.

G. S. Smith

2144. **Applications of nitrometry. IX. Determination of 2:4-dinitrophenylhydrazine.** Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (11), 1283.—When 2:4-dinitrophenylhydrazine (**I**) is treated with iodine soln. in 0·5 to 2 *N* HCl or H_2SO_4, one mole of nitrogen is liberated from one mole of **I**. The sample (20 to 80 mg of **I**) is dissolved in *N* HCl and made up to 100 ml. A 1-ml portion is introduced into a nitrometer, iodine soln. (25 per cent. in 50 per cent. KI) (0·5 ml) is then added, the whole is shaken for 1 min. and the volume of N is measured after 30 min.

K. Saito

2145. **Spectrophotometric studies of some 2:4-dinitrophenylhydrazones.** L. A. Jones, J. C. Holmes and R. B. Seligman (Philip Morris, Inc., Richmond, Va., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 191–198.—A spectrophotometric study of a series of aliphatic, olefinic, aromatic and heterocyclic aldehyde and ketone 2:4-dinitrophenylhydrazones is reported. It was found that the u.v. and visible spectra of these compounds, in neutral and basic solutions, presented a means of differentiating the type of parent carbonyl compound. A time-study of the rate of colour deterioration of the 2:4- compounds

in alcoholic solutions provided further information on the parent carbonyl structure. The i.r. structure of the 2:4- derivatives, as KBr discs, showed that the position of the N–H stretching band indicated whether the parent compound was an aldehyde or a ketone; sharper absorption bands were obtained by this technique, as compared with those by the liquid paraffin mull technique, in addition to the elimination of the C–H bands associated with liquid paraffin. Elaborate precautions were taken to obtain absolutely pure 2:4-dinitro derivatives, including chromatographic separations. The final solution in $CHCl_3$ was adjusted to be $\simeq 10$ μg per ml and the basic solutions were obtained from this by addition of ethanolic NaOH (0·25 *N*); the spectra of these basic solutions were found to be radically different from those obtained in neutral solutions. From an examination of the u.v. and visible spectra of basic derivatives of 2:4-dinitrophenylhydrazones, taken 90 min. after preparation, it has been shown that the following distinctions can be made: (*i*) aliphatic aldehydes from all other classes studied, (*ii*) aliphatic ketones from all classes studied, (*iii*) aromatic aldehydes from all classes (except olefinic aldehydes), (*iv*) aromatic ketones from all classes, when the major $\lambda_{max.}$ is < 460 mμ, in basic solution, (*v*) carbonyls containing the furan nucleus from all classes studied. A further quant. separation may be obtained from a study of the i.r. spectra showing N–H and C–H stretching at various wavelengths. The band-positions of derivatives of 2:4-dinitrophenylhydrazones, from 2 to 15 μ, are shown in tabular form for 40 different compounds from the different classes studied.

D. G. HIGGS

2146. **Paper chromatography of nitrophenylhydrazones of mono- and di-carbonyl compounds.** W. J. Schmitt, E. J. Moriconi and W. F. O'Connor (Fordham Univ., New York, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 249.—A solvent system of dibutyl ether - dimethylformamide - tetrahydrofuran is used for paper-chromatographic separation of 2:4-dinitrophenylhydrazones and *p*-nitrophenylhydrazones of mono- and di-carbonyl compounds. R_F values for 19 compounds are listed.

G. P. COOK

2147. **Chromatography of α-keto-acid 2:4-dinitrophenylhydrazones and their hydrogenation products.** A. Meister and P. A. Abendschein (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 171–173.—The 2:4-dinitrophenylhydrazones of a series of 35 α-keto acids were studied in several paper-chromatographic systems. Paper chromatography alone has a limited value in the identification of α-keto-acid hydrazones; the process of hydrogenating the hydrazones to the corresponding amino acids, followed by chromatographic separation and identification, proved successful, provided it was combined with the chromatography of the hydrazones themselves.

G. P. COOK

2148. **Paper-chromatographic identification of the 2:4-dinitrophenyl derivatives of aliphatic amines.** I. M. Lockhart (Oxford Univ., England). *Nature*, 1956, **177**, 393–394.—The technique described can be used to obtain evidence of the nature of a mixture of primary and secondary amines and ammonia. A small sample (about 10 μg) of the amine is allowed to react with 1-fluoro-2:4-dinitrobenzene and the derivative thus obtained is identified by reversed-phase chromatography on Whatman No. 1 paper, 35 cm long, impregnated with Dow Corning Silicone No. 1107. The chromatograms are developed for 16 hr. with the more polar phase obtained on mixing methanol, chloroform and water (10:10:6). Values for R_A (the ratio of the distance moved by the substance to that moved by 2:4-dinitroaniline) and R_F are given for nine derivatives which can be separated from each other. The spots are eluted from the appropriate areas with 3 ml of ethanol, and measurement of the extinction of the resulting solutions shows that the amines listed react almost quantitatively. Ammonia gives only about 50 per cent. of the expected yield. The method may have potentialities as a semi-quantitative tool, and since primary and secondary amines have different absorption maxima it can be used to corroborate whether or not the substance is derived from one or the other. By using u.v. light, 0·5 μg or less of the dinitrophenylamines can be detected.

K. A. PROCTOR

2149. **Applications of nitrometry. VII. Determination of aromatic amines.** Masaharu Yamagishi and Makoto Yokoo (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (11), 1231–1233.—The rate of diazotisation of aromatic amines, including *o*-nitroaniline and 1-naphthylamine, is markedly increased by the addition of KBr. Nitrometric determination of both can be carried out by a procedure similar to that for sulphonamides (*cf. Anal. Abstr.*, 1956, **3**, 2275). Aromatic amines having a –COOH or $-SO_3H$ group in the *para* position can be rapidly diazotised without the addition of KBr, and similarly determined. Aniline and *p*-toluidine cannot be determined by this method, since the resulting diazonium compounds are unstable. The sample (10^{-5} mole) is dissolved in 6 *N* HCl (or, when insol., in ethanol) containing KBr (0·1 g) and diazotised with KNO_2 (0° to 3° C, 2 to 10 min.). The excess of HNO_2 is decomposed with ammonium sulphamate (0·4 per cent. in 25 per cent. acetic acid, 0·1 ml) and determined in a nitrometer, with the use of NaN_3. K. SAITO

2150. **Determination of small amounts of *p*-phenylenediamine and its NN-dialkyl derivatives.** W. Massmann and G. Menge (Akad. für Sozialhyg. Arbeitshyg. und ärztl. Fortbild., Berlin-Lichtenberg). *Z. anal. Chem.*, 1955, **148** (2), 100–105.—A colorimetric determination is given for *p*-phenylenediamine and its NN-dialkyl derivatives, which are converted into coloured phenosafranines by oxidative condensation with aniline hydrochloride in the presence of $FeCl_3$. Because of parallel reactions which occur at higher concn. of *p*-phenylenediamines, not more than 20 μg of *p*-phenylenediamine itself and corresponding amounts of the other materials can be employed. In the range of concn. used, *o*- and *m*-phenylenediamines do not interfere, but benzidine, hydrazobenzene, pyrrole, formaldehyde, indamines and all strong oxidising and reducing agents must be absent. *Procedure*—The following soln. are added quickly by pipette, in the order given, to a graduated tube that is fitted with a ground glass stopper—1 ml of freshly prepared hydrazine sulphate soln. (250 μg per ml), 1 to 5 ml of the soln. to be analysed, 1 ml of HCl soln. (1:7), 1 ml of aniline hydrochloride soln. [1 vol. of aniline: 2 vol. of HCl (sp. gr. 1·19): 7 vol. of H_2O], 1 ml of $FeCl_3$ soln. [2 g of $FeCl_3.6H_2O$ and 100 ml of HCl (sp.gr. 1·19) per litre]

and 2 ml of citrate buffer (84·04 g of citric acid and 102·0 g of NaOH per litre). The mixture is well shaken, the stopper is removed and the tube is placed for $\simeq$1 hr. in a boiling-water bath. The soln. is cooled and diluted to 8 ml (if the vol. is >8 ml, a correction must be applied). The extinction of the soln. is measured, with a S53 (or S57) filter, in a 2- or 5-cm cell, with a blank as compensating soln. Standardisation curves are prepared from freshly made soln. With the exception of the hydrazine sulphate soln., all the reagents are stable for a week. J. H. WATON

2151. **Amperometric titration of pyridine with copper in the presence of thiocyanate.** Makoto Munemori (Faculty of Eng., Naniwa Univ., Sakai, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1173–1176.—The polarographic wave of Cu in 0·1 *M* KSCN was re-examined and its use for the amperometric titration of pyridine with Cu was studied. The limiting current of Cu at −0·1 to − 0·3 V *vs.* the S.C.E. is proportional to its concn. at pH 5·4 to 5·8 (acetate buffer). Pyridine (perchlorate) (12 to 80 mg per 50 ml) can be amperometrically titrated with standard $Cu(NO_3)_2$ soln. at −0·2 V in a soln. (0·1 *M* KSCN, pH 5·6) containing 1 per cent. of gelatin. Chloride ions interfere. K. SAITO

2152. **Polarographic determination of 2-cyanopyridine.** J. M. S. Jarvie, R. A. Osteryoung and G. J. Janz (Rensselaer Polytechnic Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 264–265.—2-Cyanopyridine gives a polarographic wave in ethanolic soln. buffered at a pH between 5·0 and 6·0. Recoveries of > 99·8 per cent. were obtained. G. P. COOK

2153. **Chromatography of pyrimidine reduction products.** R. M. Fink, R. E. Cline, C. McGaughey and K. Fink (Univ. Calif. Sch. Med., Los Angeles, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 4–6.—The reduction products of pyrimidine have been studied by the two-dimensional and one-dimensional techniques of Fink *et al.* (*J. Biol. Chem.*, 1952, **197**, 44). It was found that by a simple NaOH spray the intermediate dihydropyrimidine rings were opened by hydrolysis and the β-ureido acids so formed were subsequently detected by a final spray with *p*-dimethylaminobenzaldehyde (**I**) and HCl. Thus dihydrouracil and dihydrothymine were converted *in situ* into β-ureidopropionic acid and β-ureido*iso*butyric acid, respectively, which gave yellow spots with acidified **I**. Relatively accurate estimations could be made by running simultaneous chromatograms of unknown and standard solutions. D. G. HIGGS

2154. **Ultra-violet absorption spectra of some [phenyl]mercury compounds.** B. G. Gowenlock and J. Trotman (Univ. Coll., Swansea). *J. Chem. Soc.*, 1955, 1454–1458.—The marked difference in absorption between diphenylmercury and phenylmercury compounds in the 226-mμ region makes possible a determination of diphenylmercury in the presence of phenylmercury compounds without the use of dithizone (*cf. Anal. Abstr.*, 1954, **1**, 3020). N. E.

2155. **Notes on the uses of emission spectrography in the petroleum industry. II. Applications to petroleum analyses.** J. Noar (Thornton Res. Centre, Shell Res. Ltd., England). *Inst. Petrol. Rev.*, 1955, **9**, 209–212.—This is a review of applications of emission spectrography to the analysis of lubricating oils, gas oils, residual oils, metals, deposits, ashes, catalysts, etc., and to the determination of tetraethyl-lead in petrol. (49 references.) N. E.

2156. **Determination of total nitrogen in reformer charge [petroleum] stock.** R. W. King and W. B. M. Faulconer (Sun Oil Co., Norwood, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 255–258.—The method is a modification of that by ter Meulen (*Rec. Trav. Chim.*, 1924, **43**, 1248) and involves conversion of nitrogen compounds into ammonia by catalytic hydrogenation and determination of the ammonia with Nessler reagent. The sensitivity of the modification is $\simeq$ 1 p.p.m. of N and the repeatability and accuracy are of the same order in the range below 20 p.p.m. Acceptable results are obtained in the presence of considerable amounts of sulphur. The application is limited to petroleum stocks having end-points lower than 450° F. G. P. COOK

2157. **Determination of sulphuric and sulphonic acids in sour oil.** L. J. Cali and J. W. Loveland (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 224–227.—The method is a modification of that by Bacon (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 89). The H_2SO_4 is pptd. with aniline in $CHCl_3$ soln. and the aniline sulphate is filtered off, dissolved, and titrated with standard alkali. The sulphonic acids are determined by titration of the filtrate from the H_2SO_4 procedure. For sour-oil samples the standard deviation for H_2SO_4 is $\pm$ 0·007 per cent. in the range 0·01 to 0·25 per cent. and for sulphonic acids it is 0·097 per cent. in the range 3 to 8 per cent. Sulphur dioxide does not interfere. G. P. COOK

2158. **Rapid determination of nitrogen in unrefined anthracene and its refining products.** L. D. Gluzman, R. I. Melamed and D. S. Khinkis (Ural Inst. for the Chemistry of Coal). *Zavod. Lab.*, 1955, **21** (12), 1433–1435.—The anthracene material (0·1 g) in a 50-ml Kjeldahl flask is heated to complete dissolution with 10 ml of conc. H_2SO_4 (about 3 to 5 min.) and then small portions of finely divided $K_2Cr_2O_7$ (2·4 g in all) are added with stirring during the continued heating of the flask (about 5 to 7 min.). The heating is continued further (5 to 7 min.) until a bright-green paste is obtained. The temperature throughout should be 250° to 260° C. After being cooled, the contents are transferred to a distillation flask and the NH_3 is determined by the usual method. The time taken is 15 to 20 min. for decomposition and 30 min. for distillation. G. S. SMITH

2159. **Chromatographic determination of gum in fuels.** H. S. Knight, T. Skei, S. Groennings and A. C. Nixon (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 8–11.—The chromatographic separation described is based on the observation that the length of the brown stain on a column of activated silica gel is proportional to gum concn. when 1-methylnaphthalene is used as solvent and acetone as eluent. The "analyser" consists of a long capillary (precision-bore) tube (400 mm × 1 mm in diam.) at the bottom of the separator column, both of which are packed with activated silica gel (100 to 200 mesh). The soln. under examination is forced through the column under an applied air pressure of 3 to 10 lb

per sq. in. until the brown zone is well within the analyser, then its length is measured. The technique has been applied to both sol. and insol. gum in jet fuels, gas oils and, with modification, to petrols. D. G. HIGGS

2160. **Rational analysis of the mineral components of brown coal.** I. A. Khrizman (Ordzhonikidze Ufa Aviation Inst.). *Zhur. Anal. Khim.*, 1955, **10** (6), 373–377.—The minerals in brown coal are assessed by (*a*) analysis of the ash, obtained by rapid ignition, for Si, Al, Fe, Ti, Ca, Mg and SO_3, (*b*) analysis of the water extract for Ca, Mg, SO_3 and Cl, (*c*) analysis of material soluble in 10 per cent. HCl soln. for Si, Al, Fe, Ca, Mg and SO_3, (*d*) determination of moisture content, and (*e*) determination of carbonate. A method of rational analysis is described. G. S. SMITH

2161. **The use of 4-amino-4′-chlorodiphenyl hydrochloride for the determination of sulphur in coal.** H. C. Wilkinson (British Coke Res. Assoc., 74 Grosvenor St., London, England). *Analyst*, 1956, **81**, 9–11.—The coal (1 g) is burned with Eschka mixture in oxygen in a calorimeter bomb in the presence of 5 ml of 10 per cent. ammonium carbonate soln. under 25 atm. pressure. The residue is dissolved in HCl, the pH of the soln. is adjusted to 1·4 by the addition of aq. NH_3 and HCl and the vol. is adjusted to 250 ml. The SO_4'' are then determined by the method of Belcher *et al.* (*Analyst*, 1956, **81**, 4), with certain modifications in the technique. Results are given for coals ranging in sulphur content from 0·57 to 3·22 per cent. Agreement with the Eschka method is good, the mean difference being 0·03 per cent. and the time saved $\simeq$ 35 min. A. O. JONES

2162. **Determination of chlorides and thiocyanates in coal-tar pitch and its fractions.** L. D. Gluzman and R. M. Tsin (Ukraine Sci. Res. Inst. of Mining). *Zavod. Lab.*, 1956, **22** (1), 45–46.—A sample (200 g) of the pitch, well mixed after heating to between 70° and 80° C, is heated in a flask to between 80° and 90° C and shaken for 10 min. with 400 g of hot water. The solution is kept cold for 30 to 40 min. and 200 ml of the water extract are collected after filtration. For the determination of total Cl′ and SCN′, 25 to 50 ml of the extract and 20 ml of water are evaporated to dryness in a porcelain dish to remove volatile ammonium salts, the residue is dissolved in water and filtered, and the filtrate is titrated, after addition of 0·2 ml of conc. HNO_3 and 1 ml of 10 per cent. sodium nitroprusside solution, with mercuric nitrate solution, 1 ml of which corresponds to 1 mg of Cl′ or 1·63 mg of SCN′. The Cl′ are determined by boiling for 5 min. a mixture of 25 to 50 ml of the extract, a similar vol. of water, and 1·5 to 2·0 ml of conc. HNO_3, after which the cold solution is treated with 0·2 ml of conc. HNO_3 and 1 ml of 10 per cent. sodium nitroprusside solution and titrated with mercuric nitrate solution. G. S. SMITH

2163. **Photometric determination of pyridine, and β- and γ-picolines in basic tar fractions.** E. Asmus and H.-F. Kurandt (Inorg. Chem. Inst., Münster, Germany). *Z. anal. Chem.*, 1956, **149** (1–2), 3–15.—The bases are determined as the polymethine dyes made by reaction with OCl′, CN′ and barbituric acid. The dyes differ in the position (or absence) of the methyl group on the polymethine chain and thus have different light-absorption curves (*cf. Ibid.*, 1953, **139**, 81). 2:6-Lutidine does not react. The dye from pyridine ($\lambda_{max.}$ 580 mμ) has the highest absorption intensity, and the intensities of the picoline dyes are much lower and decrease in the order γ ($\lambda_{max.}$ 600 mμ), β ($\lambda_{max.} \simeq$ 500 mμ), α ($\lambda_{max.}$ 475 mμ). To determine pyridine in the α-picoline fraction of coal tar, dilute 1 g of the base to 100 ml with water, and dilute an aliquot (2 ml to 20 ml according to the pyridine content) to 1 litre. Prepare the reagent by adding, without interval, 1 per cent. KCN (1 ml), 1 per cent. chloramine T (5 ml) and 0·1 *N* HCl (2 ml) to a conical flask, and then 5 ml of the diluted sample solution. Shake and set aside for exactly 10 min., then add (from a burette) 1 per cent. barbituric acid (10 ml) and keep closed for 30 min. Determine the extinction photometrically in mercury light with filter 570 (Leitz) (*i.e.*, with the 578-mμ line). The vol. of reagent used are important, as is the continuity of operation. A calibration curve shows that the Beer - Lambert law holds. Analogous procedures are described for the determination of γ-picoline in the β-picoline fraction of tar, in technical β-picoline, and in 2:6-lutidine, and of β-picoline in the β-picoline fraction and in 2:6-lutidine. Accuracies well within ± 1 per cent. are possible in these determinations by strict adherence to instructions. J. P. STERN

2164. **Spectrophotometric determination of small amounts of anthracene in carbazole.** Takashi Yoshida, Osamu Hibino, Hajime Suzumura and Noburu Tamura (Yawata Iron and Steel Ind. Co.). *Coal Tar* (*Japan*), 1955, **7**, 114–116.—The Beckman spectrophotometer was employed for quant. analysis of anthracene in commercial carbazole by means of the key band at 358 mμ and compared with two routine chemical methods. The mean error was ± 2 per cent. The standing of the sample soln. in ethanol for longer than a day tends to decrease gradually the absorption intensity. CHEM. ABSTR.

2165. **Analysis of hydrocarbon fraction of gilsonite.** J. M. Sugihara and T. F. McCullough (Univ. Utah, Salt Lake City, Utah, U.S.A.). *Anal. Chem.*, 1956, **28** (3), 370–372.—A chromatographic method is described for separating and analysing a hydrocarbon fraction from gilsonite. By the use of a hydrated magnesium acid silicate (Magnesol) as the absorbent, a viscous yellow oil of between 4 to 8 per cent. w/w of the gilsonite was separated. This fraction was distilled into nine cuts and further separated into aromatic and non-aromatic portions. Physical and chemical analysis of these showed that the hydrocarbon fraction contained 30 to 40 per cent. of aromatics and 60 to 70 per cent. of naphthenes. G. P. COOK

2166. **Rapid determination of cellulose in viscose.** Tsugio Takeuchi and Etsuo Nakamura (Faculty of Eng., Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1955, **4** (9), 555–557.—Cellulose (**I**) is pptd. in an aq. soln. of viscose with NH_4Cl, the ppt. is dissolved in 80 per cent. H_2SO_4 and oxidised with a known excess of $K_2Cr_2O_7$. The excess of $K_2Cr_2O_7$ is titrated with Fe'' soln. in the presence of H_3PO_4, with Ba diphenylaminesulphonate (**II**) as indicator. For a rapid, quantitative pptn. of **I** a subsequent treatment of the pptd. **I** with dil. HCl (2 per cent.) is recommended. The time occupied by an estimation is $\simeq$ 1 hr. and the results agree well with those obtained by the usual gravimetric method. *Procedure*—The sample (3 g) is mixed with

water (30 ml), then treated with saturated NH_4Cl soln. (30 ml) and centrifuged. The pptd. **I** is successively treated with saturated NH_4Cl (60 ml, for 5 min.), HCl (2 per cent., 60 ml, for 5 min.) and water (60 ml). The ppt. is dissolved in 80 per cent. H_2SO_4 (30 ml) and the soln. is made up to 100 ml with water. A 10-ml portion is boiled with $K_2Cr_2O_7$ (4 per cent., 10 ml) and H_2SO_4 (72 per cent., 50 ml) for 5 min., cooled and titrated with Mohr's salt, with **II** (0·5 per cent. aq. soln., 4 ml) as indicator. K. SAITO

2167. **Determination of silicones in textile materials.** G. M. Petty (Arkansas Co., Inc., Newark, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 250–251.—The silicone-treated textile material is wet-ashed with conc. H_2SO_4 and HNO_3 and, finally, conc. $HClO_4$. The SiO_2 is then pptd. from dil. HCl soln. and is determined gravimetrically. Results agreed, within 0·02 per cent., with those obtained by a peroxide-bomb - colorimetric procedure and the average difference between duplicates was 0·007 per cent. G. P. COOK

2168. **The analysis of mixtures of surface-active quaternary ammonium compounds and polyethylene oxide type of non-ionic surface-active agents.** A. Barber, C. C. T. Chinnick and P. A. Lincoln [Milton Ind. Chem. (London) Ltd., 42–46 Weymouth Street, London]. *Analyst*, 1956, **81**, 18–25.—In the bromophenol-blue method for determining quaternary ammonium compounds, an alkaline soln. of an anionic detergent is titrated with a standard soln. of a quaternary ammonium compound in the presence of bromophenol blue and 1:2-dichloroethane. Polyoxyethylene "non-ionic" compounds interfere with the method by rendering the end-point less sharp, but this interference can be overcome by matching the end-point colour of the sample soln. with that of the 1:2-dichloroethane layer of a blank determination made with omission of the non-ionic agent. It is necessary also to add $\lessapprox$ 1·25 and $\gtrapprox$ 2·5 g of NaCl to the liquid before titration. For the assay of non-ionic surface-active agents by pptn. of a complex formed by addition of $BaCl_2$ and a heteropoly acid it was found that tungstophosphoric acid was preferable to molybdophosphoric acid as it improved the accuracy and reduced considerably the time needed for the settling of the ppt. Quaternary compounds interfere with the method, but they can be removed by shaking the soln. with a cation-exchange resin [Zeo-Karb 225(H)]. Examples of the application of these methods are given. A. O. JONES

2169. **Determination of phenol in methyl methacrylate.** Tsugio Takeuchi, Motohisa Furusawa and Yuzi Takayama (Faculty of Eng., Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1955, **4** (9), 568–571.—Phenol (**I**) (> 1 per cent.) in methyl methacrylate monomer (**II**) is acetylated with acetic anhydride (**III**) in the presence of pyridine, and the excess of **III** is titrated with alkali. The sample (<5 g, containing <0·3 g of **I**) and pyridine (0·5 ml) are added to **III** (0·6 to 0·8 g) in a stoppered bottle and heated at 100° C for 5 min. Water (10 ml) is added and the product is titrated with 0·3 *N* NaOH. Allowance must be made for any methacrylic acid (**IV**) present. When the content of **I** is <1 per cent. (but >0·001 per cent.), an aq. soln. of **II** is treated with diazotised *p*-nitroaniline (**V**), pyridine and NaOH, and the resulting orange colour is measured. Methanol, methyl 1-hydroxylactate and **IV** (< 10 mg per 100 ml) do not interfere. The sample (< 6 mg of **I**; < 1·5 g of **II** per 100 ml) is dissolved in water and a 10-ml portion is treated with **V** (1 g per litre containing 15 ml of conc. H_2SO_4; treated with $NaNO_2$ just before use until a colourless soln. is obtained) and pyridine (0·3 ml) at 10° C for > 8 min., then with 2·5 *N* NaOH (2 ml) and set aside at 10° C for 5 min. The extinction is measured at 460 mμ; Beer's law is obeyed for < 500 μg of **I** per ml. K. SAITO

2170. **Determination of methylol [hydroxymethyl] groups in phenolic resins.** G. A. Stenmark and F. T. Weiss (Shell Dev. Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 260–262.—The method is based on the condensation of hydroxymethyl groups with phenol, in the presence of an acid catalyst, to form water, which is determined with Karl Fischer reagent. Analyses of phenolic resins agreed to within 2·0 per cent. G. P. COOK

2171. **Infra-red analysis of paint vehicles based on alkyd - nitrogen resin blends.** C. D. Miller and O. D. Shreve (E. I. du Pont de Nemours & Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 200–201.—The three-component system studied in this paper consists of alkyd resin (**I**), urea - formaldehyde resin (**II**) and melamine - formaldehyde resin (**III**). The i.r. method is based on the absorbance of **I** at 5·8 μ, **II** at 6·1 μ, and **III** at 12·25 μ. A polished sodium chloride plate was uniformly coated with a thin film of resin solution, or centrifuged paint vehicle, and dried at 60° C under reduced pressure (1 mm Hg) for 1 hr. A quant. run over the range 2 to 15 μ was first made to determine the resin types present. Finally the absorbances were measured at the three wavelengths by the base-line method and the composition was calculated; since these calculations are based on absorption ratios the problem of film-thickness control is avoided. D. G. HIGGS

2172. **Volatile acids and the quality of concentrated latex.** A. S. Cook and K. C. Sekar (Chem. Div., Rubber Res. Inst. Malaya, Kuala Lumpur). *J. Rubb. Res. Inst. Malaya*, 1955, **14** (Commun. 297), 407–422.—A rapid, simplified procedure is described for the estimation of the volatile fatty acid content of latex. *Procedure*—To 50 g of latex are added 100 ml of water and 20 ml of 5 *N* H_2SO_4 in 5 ml of water. The serum is filtered from coagulum and 100 ml are mixed with 50 ml of water; after addition of anti-foaming agent, the soln. is steam-distilled at constant vol. at the rate of 50 ml in 15 min. The distillate is titrated with 0·01 *N* NaOH soln., with phenolphthalein as indicator. A blank determination is run with 50 ml of distillate from 20 ml of 5 *N* H_2SO_4 and 130 ml of water. J. L. PROSSER

2173. **The use of vanadium pentoxide and 4-amino-4′-chlorodiphenyl hydrochloride in the combustion method for the determination of total sulphur in rubber.** B. B. Bauminger (Chem. Res. Div., Dunlop Res. Centre, Birmingham, England). *Analyst*, 1956, **81**, 12–15.—Quantitative decomposition of alkali and alkaline-earth sulphates which are present in rubber compositions can be effected at 1000° C by the use of a mixture of V_2O_5 and ZnO as catalyst (Bauminger, *Kautschuk und Gummi*, 1955, **2**, WT31). For the determination of the total SO_4'' after combustion in an apparatus that

has been described elsewhere (*loc. cit.*) the method of Belcher *et al.* (*Analyst*, 1956, **81**, 4) is used, in which the insol. ppt. formed by 4-amino-4′-chlorodiphenyl hydrochloride with SO_4'' is titrated with standard alkali. For accurate results, the ppt. must be washed with a saturated aq. soln. of the precipitant. Quoted results show that there is no interference from substances often present during the analysis of synthetic rubber compounds and that the amount of S determined in these compounds is in satisfactory agreement with the calculated content. A. O. JONES

See also Abstracts 1974, 1976, 1984, 1996, 2060, 2068, 2280, 2281, 2342, 2360, 2372.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2174. **A rapid electrotitrimetric method for determining carbon dioxide combining power in plasma or serum.** M. A. Segal (Univ. Minnesota, Minneapolis, Minn., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (10), 1212–1216.—To 1 ml of serum or plasma is added 1 ml of 0·1 *N* HCl in normal saline and the soln. is mixed thoroughly for 1 min. This allows all of the HCO_3' to be released to the atmosphere as CO_2. The mixture is then titrated back with 0·01 *N* NaOH in saline to the normal pH of venous plasma (7·39 at 38° C). The correction for temp. is + 0·014 pH unit for each degree centigrade below 38° C. At 25° C the pH is 7·57.
R. S. TONKS

2175. **A self-standardisation method for flame-spectrophotometric determination of calcium in biological materials.** C. F. Rothe and L. A. Sapirstein (Ohio State Univ., Columbus, U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (9), 1076–1089.—The method, accurate to within −3 and +10 per cent., consists in adding an aliquot of the unknown to the standard, and can be performed on samples containing less than 10 μg of Ca. Samples should be diluted to give a total concn. of Ca of <0·15 milli-equiv. per litre. For plasma, a 250-μl aliquot is added to a 25-ml calibrated flask, and the same vol. of plasma with an equal vol. of $CaCl_2$ soln. (5 milli-equiv. per litre) is added to a second flask. These mixtures are then diluted to the mark with 0·01 per cent. Sterox soln. (a polyoxyalkalene fatty ester detergent). A third flask is filled as a water blank. A single determination comprises ten measurements. At 422·8 mμ the extinctions of the water, the unknown and the unknown plus added Ca are determined, also in reverse order. The background extinctions of water and unknown (also in reverse order) are determined at 420 mμ. The extinction for water is subtracted from all readings and the concn. of Ca is then calculated.
R. S. TONKS

2176. **The determination of calcium in biological fluids by flame spectrophotometry.** I. MacIntyre (Postgraduate Medical School, London). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 498–501.—The direct flame-photometric determination of Ca in serum and urine is described. Means of overcoming interferences are detailed. From a comparison of the photometric and the Kramer-Tisdall (oxalate pptn.) procedures it is suggested that the pptn. method gives low results.
P. HAAS

2177. **Photometric estimation of calcium [in serum].** R. W. R. Baker (Guy's Hospital Med. Sch., London). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 502–506.—Results obtained with a flame photometer developed for the determination of Ca in serum are presented, and details of a spray with micrometer control are given. P. HAAS

2178. **The influence of hyaluronic acid on the precipitation of calcium oxalate.** H. J. Dulce (Physiol. Chem. Inst., Freien Univ., Berlin). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 49–54.—Quantitative measurements were made of the influence of mucopolysaccharides on the pptn. of Ca oxalate, which is incomplete in the presence of these substances. The inhibiting effect is more marked at 3° C than at 37° C. At 37° C with 0·1 *N* K oxalate as the pptg. agent there is 90 per cent. pptn. after 12 hr. in the presence of 10 mg per cent. of hyaluronic acid, but when 0·01 *N* oxalate is used there is only 30 per cent. of complete pptn. during the same period. Chondroitinsulphuric acid acts similarly, but is only about half as effective. The viscosity of the mixtures of oxalate and hyaluronic acid was greater than that of the blanks which contained no mucopolysaccharide, but when the mixtures were subjected to the action of hyaluronidase the effect on viscosity disappeared before that on pptn. A protective colloid effect is assumed provisionally. These effects are considered unimportant in calcium estimations because the oxalate concn. are sufficiently high to overcome the inhibiting effect. In normal urine when the oxalate concn. is $\simeq$ 0·0015 *N* this effect may be of great importance in preventing stone formation. In oxaluria, with a 20 to 30-fold increase in oxalate concn., it is doubtful if the mucopolysaccharides increase proportionately, but they may still be effective in preventing the formation of concrements. In the experiments in this investigation, when higher oxalate concn. were used, agglomeration of the ppt. was hindered although pptn. was quantitative. F. POWELL

2179. **Flame-photometric estimation of calcium and magnesium in urine.** H. J. Dulce (Physiol. Chem. Inst., Freien Univ., Berlin). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 102–104.—By using an oxy-acetylene flame and reading Ca at 628 mμ and Mg at 383 mμ, the flame-photometric estimation of these elements is possible with an accuracy within ± 1 per cent. Owing to the influence of foreign ions, direct measurement of diluted urine is subject to errors of up to 100 per cent. *Procedure for calcium*—Acidify the urine (50 ml) with HCl and filter into a centrifuge tube. Add freshly dissolved ammonium oxalate (1·5 g) and heat to 70° C. Add aq. NH_3 dropwise, until the pH is 6·0. Set aside for 1 hr. at room temp. Centrifuge and wash the deposit with 0·1 per cent. ammonium oxalate. Dissolve in 12·5 per cent. HCl (5 ml) and make the vol. up to 50 ml with water. This soln. is diluted 1:10 for the flame-photometer reading. *Procedure for magnesium*—Add 10 per cent. $(NH_4)_2HPO_4$ (10 ml) to the supernatant liquid and the washings from the original pptn. and then add conc. aq. NH_3 soln. until the pH is 6·5 to 7·0. When crystals

begin to appear, add a further 3 ml of conc. aq. NH_3 soln. Set aside for 12 hr. at room temp. Wash twice with 1 per cent. aq. NH_3 and dissolve the ppt. in 12·5 per cent. HCl (5 ml) and make the soln. up to 50 ml. This is used directly for flame photometry. Conditions for precipitating must be strictly adhered to or errors of up to 35 per cent. may occur. Addition of 25 per cent. of *iso*propyl alcohol is valuable for increasing magnesium emission when concn. are low, but is not desirable when the concn. of Mg is > 10 mg per cent.

F. POWELL

2180. **Hydrocyanic acid formation as a source of error in chloride estimations by Van Slyke's method.** E. Schütte and L. Kiesow (Physiol. Chem. Inst., Freien Univ., Berlin). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 96–101.—The determination of chloride by back-titration with KSCN after digestion with $AgNO_3$ and HNO_3 is subject to errors owing to the formation of HCN from the proteins. Tyrosine, tryptophan and phenol are the principal causes of interference in this respect. When cyanide determinations were carried out on casein digested with HNO_3 it was found that the chloride figures were subject to errors of up to 60 per cent. Preliminary heating with alkali (Sunderman and Williams, *J. Biol. Chem.*, 1931, **92**, 99) lowers the cyanide value for tyrosine, raises it for tryptophan and has no effect on cyanide formation with phenol. The effect on proteins will therefore vary with the relative proportions of tyrosine and tryptophan. F. POWELL

2181. **Potentiometric titration of chlorides in biological fluids.** A. Jordan. *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 522–529.—A method has been developed for the direct titration of chlorides in biological fluids, with silver nitrate: the end-point is detected by means of a direct-reading potentiometer. The apparatus is illustrated and circuit diagrams are given. P. HAAS

2182. **Potentiometric determination of chlorides in biological fluids. Microgram analysis.** M. G. Sanz and T. Brechbühler (Univ. Hospital, Geneva, Switzerland). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 530–536.—A description is given of a simple system for the determination of a few micrograms of Cl′ in the presence of proteins. The high potential jump at the equivalence point permits a normal valve potentiometer to be used. A new ultramicro burette is described. P. HAAS

2183. **Experiences with an ^{131}I excretion test, using small radioactive doses.** K. F. Stöa (Biochem. Lab., Univ. Clinic, Bergen, Norway). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 326–333.—A method for measuring small amounts (about 8 μC) of excreted radioactive I in urine, after oral administration, is described. P. HAAS

2184. **Spectrochemical determination of trace quantities of cobalt in animal tissues.** R. G. Keenan and J. F. Kopp (U.S. Dept. Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 185–189.—The two spectrochemical methods developed for the determination of traces of Co in tissues of animals exposed to cobalt metal fumes are (*i*) direct determination on the ash, when the sample contains 0·025 μg of Co per g of fresh tissue in excess of that present in normal tissue, and (*ii*) the concn. method, when chemical separation, with $Al(OH)_3$ as carrier, is employed; the degree of sensitivity for this method is 0·001 p.p.m. per 30-g sample of fresh tissue. The average error over the range 0·006 to 0·1 μg is $\simeq -$ 6 per cent., but greater accuracy is attained by this method than by (*i*). Palladium is employed as internal standard since it has not been found in natural tissues and is also unaffected by variation in Co concn. A LiCl - graphite buffer mixture is employed (in the ratio 0·4:1·0) which, when mixed with an equal amount (5·0 mg) of $Al_2O_3 + Co_3O_4$ ash and 0·5 μg of Pd, is transferred to the hollow cup of the graphite electrode and dried. The electrodes are burnt in a 220-V d.c. arc operated at 9 amp. with a 10-mm gap for 25 to 35 sec. (or until burn-out). The transmission values of the Co 3453·5 A and Pd 3460·8 A lines are measured, corrected for background adjacent to the Co line and the concn. of Co is obtained by reference to calibration curves. D. G. HIGGS

2185. **Determination of methanol in body fluids.** F. Stratton (Harvard Med. Sch., Boston, Mass., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (9), 1071–1075.—The method depends on the oxidation of steam-distilled aliquots of blood with permanganate and phosphoric acid, bleaching with saturated oxalic acid soln. and evaporation to dryness with chromotropic acid followed by further heating with conc. sulphuric acid. The resulting solution is diluted with water and the extinction is read at 570 mμ. The colour is stable and extinction readings are linear to a level of 1·5 ml of 1:100 methanol in the 10-ml aliquot. At higher concn. the colour production drops. Ethanol does not interfere with methanol determinations.

R. S. TONKS

2186. **A simple colorimetric method to determine sugar in urine.** F. Moya and J. Dewar (Victoria Gen. Hosp., Halifax, Nova Scotia). *J. Lab. Clin. Med.*, 1956, **47** (2), 314–319.—It is considered that the high sensitivity of Benedict's qual. procedure may be due to false positive reactions, and a rapid modified quant. test is proposed. *Procedure*—To 0·2 ml of urine in the bottom of a Folin - Wu sugar tube add 4·0 ml of Benedict's qual. reagent, prepared with an accurately weighed amount of copper sulphate. Mix gently and heat in a boiling-water bath for 8 min. Cool in cold water, dilute to 25 ml with water, filter if necessary through a Whatman No. 42 paper and measure the colour due to residual Cu^{++} at 650 mμ against water. Calibration with 0·2 ml of standard glucose solution is rectilinear for concn. up to 3·5 per cent. The procedure may also be used as an improved qual. test.

W. H. C. SHAW

2187. **Simplified paper-chromatographic method for separation of glucose and fructose in urine.** A. S. Cohen and N. Kantor (Boston City Hosp., Boston, Mass., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (11), 1328–1330.—The solvent used is *n*-propanol - water (3:1) and this travels $\simeq$ 14 cm in 4 hr. on Whatman No. 1 filter-paper by the ascending technique. The urine is spotted on the paper by means of capillary pipettes calibrated to deliver 0·02 ml. A 1:3-dihydroxynaphthalene spray (0·2 per cent. in ethanol plus 0·1 vol. of conc. H_3PO_4) makes the detection of glucose (R_F 0·35) and fructose (R_F 0·44) relatively simple. Glucose appears as a blue spot and fructose as a distinct red - purple spot on the paper, after spraying and

drying for 5 to 10 min. at 90° C. Complete separation of these two hexoses can be effected by an overnight chromatogram. R. S. TONKS

2188. **The estimation of sorbose in blood.** K. Täufel and K. Müller (Inst. f. Ernährungsforsch. Potsdam-Rehbrücke). *Biochem. Z.*, 1955, **327**(4), 267–272.—Sorbose may be detected qualitatively in plasma by descending paper chromatography in butanol - acetic acid - H_2O (4:1:5) for 3 to 4 hr. with subsequent development of the spots with resorcinol - trichloroacetic acid reagent (10 ml of a 1 per cent. ethanolic soln. of resorcinol and 90 ml of a 40 per cent. solution of trichloroacetic acid); a red colour appears after heating for 5 min. at 105° C. Other ketoses which might interfere do not normally appear in blood, the amount of fructose being too low to show this reaction. An approximate quant. assessment of amounts in the region of 20 mg per cent. of sorbose can be made by comparing the intensity of the colour reaction with that of standard sorbose solutions. A quant. determination of sorbose in blood can be made after the removal of glucose and fructose by incubation with a yeast suspension, subsequent pptn. by sodium tungstate of the proteins, and estimation of the remaining sorbose in the protein-free filtrate by the Hagedorn and Jensen method. G. W. CAMBRIDGE

2189. **Chromatography of polysaccharide hydrolysates.** E. Kulonen. *Suomen Kem., B*, 1955, **28**, 103–105.—In a previous publication (*Scand. J. Clin. Lab. Invest.*, 1952, **4**, 189) the author noted the occurrence of dark spots on the phenol chromatograms of hydrolysates of umbilical cord and attributed them to the presence of glycine and serine; this suggestion is now abandoned in favour of the opinion that the spots are in some way connected with the formation of humin, the presence of which was established by showing that it contained carbonyl groups capable of reacting with 2:4-dinitrophenylhydrazine. P. HAAS

2190. **Determination of cyanide in biological fluids by microdiffusion analysis.** M. Feldstein and N. C. Klendshoj (Univ. of Buffalo, Buffalo, N.Y., U.S.A.). *Canad. J. Med. Technol.*, 1955, **17**, 29–32.—A rapid method for the estimation of cyanide in biological fluids is based on the diffusion of HCN from the outer cell of a Conway unit into 0·1 *N* NaOH in the inner cell. The HCN absorbed is converted into NCCl with NaH_2PO_4 and chloramine T, and a red colour is developed by adding pyridine - barbituric acid reagent. The colour is measured spectrophotometrically. The method is sensitive for concn. of 0·025 to 25 μg per ml with an accuracy within 4 per cent. Diffusion was complete in 3 hr. Normal cyanide levels were found to range from 0 to 10 μg per 100 ml of blood. Mild exposure to cyanide fumes increased the blood levels shortly after exposure. Fatal exposures showed $>$ 700 μg in 100 ml. (*Cf. Anal. Abstr.*, 1954, **1**, 2753.) CHEM. ABSTR.

2191. **Determination of blood urea nitrogen using a simple stabilising reagent.** H. V. Connerty, A. R. Briggs and E. H. Eaton (V.A. Hosp., Wilmington, Del., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (11), 1321–1325.—One drop of a 2 per cent. aq. soln. of I added to a diluted blood filtrate or to Nessler reagent before use completely eliminates turbidity and drift in extinction for at least 1 hr. One ml of whole blood is diluted with 0·1 ml of a 10 per cent. glycerol - urease soln. and incubated at room temp. for 20 min.; a Folin - Wu blood filtrate is prepared and 1 ml is diluted to 10 ml with water. R. S. TONKS

2192. **Simple micro-determination of uric acid.** C. A. Dubbs, F. W. Davis and W. S. Adams (Veterans Admin. Center, Univ. of Calif. Med. Center, Los Angeles, Calif., U.S.A.). *J. Biol. Chem.*, 1956, **218** (1), 497–504.—Uric acid in urine and serum is determined by a modification of the Kalckar method (*Brit. Abstr. C*, 1947, 92), which utilises the specific decrease of uric acid extinction at 292 mμ in the presence of uricase. A single determination takes 2 to 4 hr., and a sufficiently dil. uricase prep. is used to ensure that uric acid destruction proceeds slowly enough to enable a single reliable reading of the initial extinction to be taken. Although a longer time is required, the method is superior to that of Praetorius and Poulsen (*Scand. J. Clin. & Lab. Invest.*, 1953, **5**, 273). J. N. ASHLEY

2193. **Direct determination of uric acid using uricase.** T. V. Feichtmeir and H. T. Wrenn (School of Med., Univ., Calif., San Francisco). *Amer. J. Clin. Path.*, 1955, **25** (7), 833–839.—The method described, in which uricase and the measurement of the change in extinction at 293 mμ are used, is said to have a high degree of accuracy. R. S. TONKS

2194. **Determination of uric acid in serum by a carbonate method.** W. T. Caraway (Rhode Island Hosp., Providence, R.I., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (7), 840–845.—Two stable reagent soln., sodium carbonate and tungstophosphoric acid, are added directly to a tungstic acid filtrate of serum to develop a colour. *Procedure*—To 1·0 ml of serum add, with mixing, 9·0 ml of precipitating reagent (10 g of sodium tungstate in 800 ml of water with 100 ml of $\frac{2}{3}$ *N* H_2SO_4) and centrifuge. Transfer 5·0 ml of supernatant liquid to a test-tube and use 5 ml of water in a second tube for a blank. Add Na_2CO_3 soln. (1·0 ml of 10 per cent.) to each tube in addition to 1·0 ml of dilute tungstophosphoric acid (10 ml of Folin - Denis reagent to 100 ml of water). Allow to stand for 30 min. at room temp. and measure the extinction at 700 mμ. The concn. of uric acid in the serum is derived from a calibration curve. R. S. TONKS

2195. **Indol-3-ylacetic acid in human urine after muscular effort.** J. A. Kral, A. Zenisek and I. Stolz (Karlovy Univ., Prague, Czechoslovakia). *Biochim. Biophys. Acta*, 1956, **19** (1), 169.—Preliminary separation of indol-3-ylacetic acid from 15 ml of urine acidified with acetic acid is effected on 400 mg of a mixture of equal parts of charcoal and silica, which is then eluted with 10 ml of *n*-butanol - water - aq. NH_3 - methanol (2:15:2:1). The eluate is evaporated to dryness, the residue is dissolved in 0·5 ml of water and 25 μl are chromatographed on paper. Development is with *n*-butanol - aq. NH_3 - water (15:1:4), for which the R_F value is 0·47. Indol-3-ylacetic acid is detected by the red colour formed on spraying with 5 per cent. $FeCl_3$ in acetic acid. W. H. C. SHAW

2196. **Excretion of pyrimidine reduction products by the rat. [Determination of β-ureido acids and dihydropyrimidines in urine.]** K. Fink (Investigative Med. Serv., Veterans Admin. Hosp., Long Beach, Calif., U.S.A.). *J. Biol. Chem.*, 1956, **218**

(1), 9–14.—The chromatographic method for the detection of β-ureido acids and dihydropyrimidines (Fink *et al.*, *Fed. Proc.*, 1954, **13**, 207) is developed into a method for the determination of these substances. The urine samples are spotted on to filter-paper, and the β-ureido acids are detected by spraying with *p*-dimethylaminobenzaldehyde. Hydrolysis of the dihydropyrimidines on the paper is effected by spraying with 0·5 *N* NaOH and drying for at least 30 min., when the paper is treated with *p*-dimethylaminobenzaldehyde. Densitometric measurements of the coloured spots are made at 440 mμ; a formula is given for calculating the amount of substance. J. N. ASHLEY

2197. **The fluorimetric determination of porphyrin.** K. Weber and F. Valić (Yugoslav. Akad. Sci., Zagreb, Yugoslavia). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 556–562.—In discussing the use of fluorimetric apparatus, emphasis is laid on the need for suitable illumination and correct combination of filters. Standards of soln. of rhodamine B adsorbed on filter-paper are recommended in place of those of coproporphyrin. P. HAAS

2198. **Special counter-current methods for the analysis of mixtures of porphyrins.** J. Otero de la Gandara and J. Tamarit Torres. *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 637–639.—The mixture of two porphyrins of known distribution coeff. (*K*) is resolved by means of a formula which gives the *K* of the mixture as a function of the percentage of each of the components; for this a distribution of four transfers suffices. A mixture of three porphyrins of unknown *K* requires eight transfers; by plotting the curves of the two substances having the largest and smallest factors the third component can be found. P. HAAS

2199. **A simple apparatus for the semi-quantitative determination of coproporphyrin in urine.** W. F. Donath. *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 551–555.—The simple fluorimetric method described for the semi-quantitative determination of coproporphyrin in urine is suitable for the approximate determination of lead poisoning. A scale of specially prepared fluorescent papers has been devised by means of which the fluorescence of an ethereal soln. of a coproporphyrin (up to 5000 μg per litre) can be matched. P. HAAS

2200. **Simple micro-method for determination of bilirubin in plasma.** J. H. Graham. *Amer. J. Med. Sci.*, 1955, **230** (6), 633–635.—Six heparinised capillary tubes 75 mm long are two-thirds filled with blood from the heel of an infant and then sealed at one end. The tubes are centrifuged at 11,000 r.p.m. for 4 min., then broken at the junction of the plasma and packed cells and the plasma is blown into a watch-glass. The plasma (0·1 ml) is recovered with a serological pipette and 0·9 ml of water is added. The diluted plasma (0·1 ml) is transferred to each of 2 micro cuvettes, to which are added 0·5 ml of methanol and 0·1 ml of a soln. containing sulphanilic acid (1 g) dissolved in conc. HCl (15 ml) and diluted to 1 litre, and 0·1 ml of diazo reagent. After 30 min., the percentage transmission is read at 540 mμ. Values are calculated from a standard curve.
R. S. TONKS

2201. **The nature of cholesteryl esters in human blood serum.** C. Michalec (Univ. Hosp., Prague, Czechoslovakia). *Biochim. Biophys. Acta*, 1956, **19** (1), 187–188.—Cholesterol and its esters are chromatographed on Whatman No. 3 paper dipped in 10 per cent. v/v liquid paraffin in ether and the ether is allowed to evaporate. The sample (200 μg) is placed on the paper, which is then developed by the ascending technique with acetic acid - chloroform - liquid paraffin (65:25:10, v/v) for 12 to 15 hr. at about 20° C. After being dried at 70° to 100° C the chromatogram is dipped in 10 per cent. ethanolic tungstophosphoric acid and heated at 100° to 110° C for 5 min. to develop purple spots, or placed between two glass plates and immersed in 20 per cent. v/v H_2SO_4 in acetic anhydride for 20 min. (green spots). Details are given for the preliminary isolation of cholesterol and its esters from blood serum and for the quantitative application of the method. W. H. C. SHAW

2202. **Ultra-micro determination of acetylcholine in cerebrospinal fluid.** R. P. MacDonald, C.Gerber and A. Nielsen (Harper Hosp., Detroit, Mich., U.S.A.). *Amer. J. Clin. Path.*, 1955, **25** (12), 1367–1370.—Acetylcholine reacts stoicheiometrically with hydroxylamine in an alkaline soln. to form hydroxamic acid. The colour produced is measured in an excess of Fe^{+++} at 540 mμ. *Procedure*—Add the sample (1 ml) to each of two tubes (*A* and *B*). Tube *A* contains 100 μl of *N* HCl and 100 μl of neostigmine bromide soln. (1:440) as preservative. Set both tubes aside for 10 min. at room temp. to allow hydrolysis of acetylcholine in tube *B*. Add preservative to tube *B* and also to a third tube (*C*) to which add 100 μl of standard acetylcholine soln. (10 mg per cent.). Transfer 250 μl of each sample to separate test-tubes, add 50 μl of freshly prepared alkaline hydroxylamine soln. (equal parts of 2 *M* hydroxylamine hydrochloride and 3·5 *N* NaOH soln.) and mix. Add 25 μl of 4 *N* HCl, mix and allow to stand for 1 min. Then add 25 μl of $FeCl_3$ soln. (0·37 *M*), mix and allow to stand for 10 min. then transfer to micro cuvettes and measure the extinction of the purple-brown colour. R. S. TONKS

2203. **A quantitative chemical test for "microscopic haematuria."** H. W. Balme, A. E. Dormer and L. Rawlings (St. Bartholomew's Hosp., London). *Brit. Med. J.*, 1956, 612–614.—Add 5 ml and 10 ml of urine to separate tubes and centrifuge at 3000 r.p.m. for 10 min. Remove from each all but 0·2 ml of the supernatant and make up to 1 ml with water. Add 0·2 ml of 30 per cent. acetic acid, 1 ml of alcoholic amidopyrine and 3 drops of 20-vol. H_2O_2. Shake the tubes and note the production of a lilac colour within 3 min. If neither is positive the urine contains < 5000 red cells per ml; if the ppt. from 10 ml is positive and that from 5 ml is negative it contains 5000 red cells per ml. If both are positive prepare serial dilutions with 5 ml of normal urine (red-cell free) or 5 ml of normal saline as diluent adding 5 ml of test urine to the first tube, mixing and transferring 5 ml to the second tube and so on until the dilutions range from 1:2 to 1:64 (6 tubes). Carry out the test on each tube and note the greatest dilution that just gives a positive reaction; calculate the red blood cells per ml by multiplying the dilution factor by 10,000. If all the tubes are still positive the urine is approaching macroscopic blood level and contains more than 1,000,000 red blood corpuscles per ml.
H. F. W. KIRKPATRICK

2204. **Spectrophotometric determination of total haemoglobin in plasma.** K. B. McCall (Dept. of Health, Lansing, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 189–191.—A simple method has been developed for the spectrophotometric determination of total haemoglobin in plasma and is based on three facts—(*i*) haemoglobin is readily converted into methaemoglobin (**I**) by $Fe(CN)_6'''$ at pH 6·6, (*ii*) **I** is readily converted into cyanomethaemoglobin (**II**) on addition of NaCN, and (*iii*) both **I** and **II** obey Beer's law over a wavelength range of 540 to 550 mμ. Calibration curves may be prepared from standard solutions, suitably diluted, of whole blood whose total haemoglobin content has been determined by standard methods. A plasma sample (10 ml), containing 1 to 10 mg of haemoglobin, was found most suitable for a 1-cm cell. The absorption of the solution was measured at a specific wavelength between 540 and 550 mμ after conversion of the haemoglobin into **I**, and again at the same wavelength after conversion into **II**; the difference between **II** and **I** then gave a value which was proportional to the haemoglobin content of the blood. The method has the advantage of simplicity, stable reagents, stable colours and a fair degree of precision and accuracy. D. G. HIGGS

2205. **Spectrophotometric determination of haemoglobin oxygen saturation.** L. Klungsöyr and K. F. Stöa (Univ. Clinic, Bergen, Norway). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 571–578.—A rapid and accurate method for the spectrophotometric determination of oxygen saturation in slightly diluted haemolysed blood, based on the method of Drabkin and Schmidt (*J. Biol. Chem.*, 1945, **157**, 69), is described. A simplification consists in measuring only the relative density in the unknown sample at two different wavelengths (*cf.* Lambrechts *et al.*, *Acta Biol. Belg.*, 1942, **2**, 109). As a result it is found that the method gives an average value for arterial oxygen saturation in normal individuals of 98 per cent., which is 3·3 per cent. greater than the value reported by Storstein (*Acta Med. Scand. Suppl.*, 1952, 269), who used a manometric method. P. HAAS

2206. **Haemoglobin solutions for electrophoresis.** V. N. Tompkins. *Amer. J. Clin. Path.*, 1955, **25** (12), 1430–1431.—Centrifuge oxalated, heparinised or citrated blood, remove the plasma and add water in vol. equal to the mass of cells. Shake the soln. to haemolyse. Add 0·1 vol. of Pb acetate soln. (10 g in 90 ml of boiling water and 10 ml of hot barbitone buffer, pH 8·6 and 0·5 *M*). After 30 min., centrifuge at 2000 r.p.m. for 10 min. Add one drop of phosphate soln. (half-saturated) and centrifuge again for 3 min. Haemoglobin soln. prepared in this manner resolve sharply into constituent components on electrophoresis. R. S. TONKS

2207. **The estimation of some different kinds of human haemoglobin.** P. C. van der Schaaf and T. H. J. Huisman (Univ. Groningen, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 563–570.—An investigation of the methods for determining foetal (Hb_f) and sickle-cell (Hb_b) haemoglobins in the presence of adult haemoglobin (Hb_a) has led to the conclusion that, for the determination of Hb_f, the alkali denaturation method is not sufficient in the presence of Hb_a and Hb_b haemoglobins. A combination of four methods based on differences in alkali denaturation, electrophoretic behaviour, u.v. absorption and amino-acid composition, provides a more definite answer to the presence of this protein. Only electrophoretic measurements can be used at present for the detection and determination of Hb_b. By the use of the four different methods it appears that the alkali-resistant fraction, sometimes found in the blood of patients with sickle-cell anaemia, is not foetal haemoglobin. P. HAAS

2208. **The determination of the higher saturated fatty acids in blood serum.** N. A. Pikaar (Univ. Hospital, Univ. Utrecht, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 627–632.—In the method described for determining higher even-numbered straight-chain fatty acids, only 2 to 4 ml of blood are required. Before the determination the serum has to be extracted with ethanol - ether and then saponification is carried out with *N* Na ethoxide, in the presence of quinol to prevent oxidation, and with subsequent drying of the residue in a stream of N. After saponification and removal of the unsaponifiable residue the free fatty acids are titrated with about 0·004 *N* Na ethoxide. As unsaturated acids interfere with any subsequent separation of the higher saturated acids by chromatography, they must be oxidised by alkaline $KMnO_4$. The standard error of the determination is about 5 per cent. P. HAAS

2209. **An aluminium hydroxide - molybdoarsenic acid method for the determination of minute quantities of tissue catechol amines.** J. M. B. Bloodworth and E. von Haam (State Univ., Columbus, Ohio, U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (2), 308–315.—The method described is suitable for the determination of catechol amines (adrenaline and noradrenaline) (**I**) in extracts from $\ll$ 2 g of tissue. Preliminary concn. and separation from some interfering substances is by adsorption on alumina at pH 7·5; **I** are then determined from the difference in colour produced by reduction of molybdoarsenic acid with and without destruction of **I** by treatment with excess of alkali at 100° C. The use of the method for determining **I** in heart muscle after the administration of adrenaline or noradrenaline is described. W. H. C. SHAW

2210. **Incorporation of organic (protein) and inorganic (sulphate) sulphur in cartilage, bone and teeth.** H. D. Cremer and G. Dittmann (Physiol.-chem. Inst., Johannes Gutenberg Univ., Mainz, Germany). *Biochem. Z.*, 1956, **327** (5), 377-382.—Protein, chondroitinsulphuric acid and sulphate can be separated by paper electrophoresis for 5 hr. at 4 to 5 V per cm by the use of 0·1 *M* barbitone buffer at pH 8·6. Chondroitinsulphuric acid may then be stained with toluidine blue or Gentian violet and protein by the usual methods. Application of this method to the study of the distribution of ^{35}S in tissues is reported. G. W. CAMBRIDGE

2211. **Chondroitinsulphuric acid in cartilage, bone and teeth. [Estimation of chondroitinsulphuric acid and hexosamine.]** G. Dittmann and H. D. Cremer (Physiol.-chem. Inst., Johannes Gutenberg Univ., Mainz, Germany). *Biochem Z.*, 1956, **327** (5), 368–376.—Chondroitinsulphuric acid may be estimated by spotting the solution on filter-paper and staining with either 0·5 per cent. toluidine blue in 10 per cent. acetic acid solution or a 0·5 per cent. solution of Gentian violet in 10 per cent. acetic acid for 10 to 15 min., the excess of stain being removed by washing with a mixture of methanol, acetic acid and water (50:10:40), and, for the toluidine blue

method, by two further washings in 10 per cent. acetic acid. The photometric - planimetric evaluation is then made by the usual method. The toluidine blue method may be used for the estimation of 100 to 600 μg of chondroitinsulphuric acid in 0·03 ml of fluid. By an elution technique the Gentian violet method can be used for the estimation of 20 to 100 μg of chondroitinsulphuric acid in 0·03 ml of fluid, the error being about 3 per cent. The influence of the amount of acetylacetone and the time of reaction in the hexosamine determination by the method of Einbinder and Schubert (*J. Biol. Chem.*, 1950, **320**, 273) is reported. By modification of the method, amounts of 0·1 to 20 mg can be estimated, the error being up to $\pm$ 3 per cent. G. W. CAMBRIDGE

2212. **Quantitative infra-red spectroscopy of deoxyribonucleic acid in the fractional milligram range.** H. P. Schwarz, R. Childs, L.Dreisbach and S. V. Mastrangelo (Div. of Biochem. Philadelphia Gen. Hosp., Pa., U.S.A.). *Science*, 1956, **123**, 328–329.—Aqueous soln. of highly polymerised deoxyribonucleic acid (**I**) were mixed with dil. soln. of KBr to give exact amounts (20 to 300 μg) of **I** in 10 ml of 1·2 per cent. KBr; the soln. were frozen quickly in "dry-ice" - acetone and lyophilised by freeze-drying. The frozen dried material (50 mg) was transferred to a steel die ($\frac{1}{4}$ in. diam.), the die was evacuated to about 1 mm of Hg and transparent discs of 1 mm thickness were pressed in a Carver press. Infra-red spectroscopy of the discs was carried out with a Beckman I.R.2 spectrometer equipped with a beam-condenser unit comprised of a system of silver chloride lenses. Discs containing 9, 18, 27, 36, 54 and 72 μg of **I** were examined for the bands at 8·1 μ, 9·80 μ and 10·30 μ. Beer's law was followed at all concn. in each band. At concn. of **I** of $<$ 36 μg the percentage average deviation of the extinction coefficients was $\pm$ 3 to $\pm$ 4·2 for all three bands. At concn. of **I** $<$ 36 μg this deviation increased in the weaker bands (9·80 μ and 10·30 μ) but remained at $\pm$ 3 in the strong 8·1-μ band. H. F. W. KIRKPATRICK

2213. **Studies in histochemistry. I. Determination of nucleic acids in microgram amounts of tissue.** J. F. Scott, A. P. Fraccastoro and E. B. Taft (Mass. Gen. Hosp., Boston, Mass., U.S.A.). *J. Histochem. Cytochem.*, 1956, **4** (1), 1–10.—The method depends on the u.v. absorption of the purine and pyrimidine constituents of the nucleic acids; thus no colour reaction or ashing procedure is needed and the sample is still available for further procedures. In order to separate the deoxyribonucleic acid (DNA) from the ribonucleic acid (RNA), treatment with dil. alkali for 1 hr. at room temp. renders the RNA acid-soluble while the DNA remains acid-insoluble. The principle of the method of Ogur and Rosen (*Arch. Biochem.*, 1950, **25**, 262) was used to release the DNA from the acid-insoluble complex with protein, but a reduction in time and temp. of the acid hydrolysis had to be made to avoid serious errors. The results were in good agreement with the Scheider:Schmidt-Thaunhauser macro-method. N. E.

2214. **A micro-method for the estimation of ammonia, especially in protein hydrolysates.** F. G. Fisher and H. Bohn (Chem. Inst., Univ. Würzburg, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (4–6), 278–282.—The method consists in collecting the NH_3 by diffusion into a drop of H_2SO_4; NaCl and MgO are used to promote liberation of the NH_3. It is claimed that complete recovery of NH_3 with no interference from amino acids is thus obtained. The method is suitable for determining the ammonia content of 30 to 100 μl of 1 per cent. protein hydrolysate, with an accuracy of $\pm$ 1 per cent. It is, however, suggested that determinations for standards, blanks and tests be all carried out in sextuplicate. *Procedure*—Erlenmeyer flasks (15 ml capacity) fitted with rubber stoppers carrying a glass rod are used. The lower end of the glass rod contains a small cavity capable of holding $\simeq$ 0·05 ml of liquid. Place one drop of 0·5 *N* H_2SO_4 in the cavity and add the sample (100 μl) and water (400 μl) to the flask. For very small quantities of sample, place 10 to 20 μl on filter-paper (about 2 cm $\times$ 1·5 cm) and dry with warm air. Place the paper in the flask and add 600 μl of water. The distance between the drop and the liquid should not be more than 1 cm. Then add a tablet of 0·5 g of a mixture of NaCl and MgO (5:1, w/w). Stopper and shake the flask to disintegrate the tablet and set aside for 15 to 20 hr. to allow the NH_3 to diffuse into the H_2SO_4. Then transfer the drop to a tube containing 1 ml of citrate buffer (pH 5·0) and add 1 ml of 1 per cent. ninhydrin in 2-methoxyethanol and 1 drop of 0·01 *M* KCN. Heat the mixture in a boiling-water bath for 30 min., cool it in water for 5 min. and then add 5 ml of methanol - water (3:2, v/v). Measure the extinction at 570 mμ. F. POWELL

2215. **Colorimetric ninhydrin reaction for measurement of α-amino nitrogen.** H. Kalant (Univ. Toronto, Toronto, Canada). *Anal. Chem.*, 1956, **28** (2), 265–266.—The colorimetric method of Cocking and Yemm (*Anal. Abstr.*, 1955, **2**, 181) was applied to the measurement of free amino nitrogen in tungstic acid filtrates of plasma. Excess of ninhydrin or of cyanide reagent affects the colour development, as does the presence of peroxides. Metal salts do not interfere in the presence of a citrate buffer. Recovery of added amino acids from plasma samples was 97 $\pm$ 4·0 per cent. G. P. COOK

2216. **Critical observations on clinical paper chromatography of amino acids.** H. Schönenberg (Univ. Kinderklinik, Münster, Germany). *Klin. Wochschr.*, 1956, **34** (9–10), 269–272.—The factors that minimise the quantitative significance of paper chromatography of amino acids in urine are discussed. The author concludes that results given by present procedures are of only qualitative significance, or semi-quantitative in the detection of pathological amino-acid excretion. H. F. W. KIRKPATRICK

2217. **Specific identification of amino acids and vitamins by refractive index and eutectic temperature. Application to paper chromatography and as a confirmatory test.** A. Lacourt, N. Delande and G. Depaduwa (Univ. of Brussels, Belgium). *Anal. Chim. Acta*, 1956, **14** (2), 100–108.—The methods of identification described are applicable to the amounts of substance that can be recovered from a chromatographic spot on paper by sublimation (for amino acids) or by elution and crystallisation (for amino acids and vitamins). Refractive indices are determined by the immersion method with a polarising microscope [*cf.* Lacourt, *J. Pharm. Belg.*, 1953, (11–12), 552]. Values for 38 amino acids and 14 vitamins and related substances are listed. Melting

points for binary eutectics are observed with a polarising microscope (*loc. cit.*), and values are given for 18 amino acids and 9 vitamins and related substances. W. C. JOHNSON

2218. **A method for the quantitative determination of C-terminal amino-acid residues.** S. W. Fox, T. L. Hurst, J. F. Griffith and O. Underwood (Iowa State College, Ames, U.S.A.). *J. Amer. Chem. Soc.*, 1955, **77**, 3119–3122.—A carboxoid method based on thiohydantoin formation is described. The method has been applied to amino acids, dipeptides, tripeptides and lysozyme. Advantages over other methods of C-terminal estimation are stereospecificity, quantitative applicability, and ease of operation. When applied to lysozyme, one C-terminal leucine residue was found. C. A. SLATER

2219. **The identification of phenylalanine on paper chromatograms.** A. E. Pasieka and J. F. Morgan (Dept. Nat. Health and Welfare, Ottawa, Canada). *Biochim. Biophys. Acta*, 1956, **19** (2), 366–371.—The position of phenylalanine on paper chromatograms of amino acids may be found by treating the chromatogram with ninhydrin reagent, heating to 110° C to develop the normal colour and further treatment with aq. $NaHCO_3$ (0·15 to 10 per cent.), or with one of the other mild alkalis specified, and redrying. Applied in this way, the blue colour obtained (max. at 560 mμ in *n*-butanol) in the test is specific for 5 μg or more of phenylalanine, irrespective of its optical rotation, and is not given by derivatives or peptides of phenylalanine. The test can be applied when separation from other amino acids is incomplete. W. H. C. SHAW

2220. **The biological assay of L-methionine using a mutant of *Escherichia coli* Strain K-12.** B. Ruebner (Postgraduate Med. Sch., London, W.12). *J. Lab. Clin. Med.*, 1956, **47** (1), 140–144.—A turbidimetric microbiological method is described for the determination of L-methionine in plasma, with a simple medium and a methionine-requiring *E. coli* mutant as test organism. The method is satisfactory for levels of methionine up to 5 μg per ml in the medium, and its use in the investigation of abnormal methionine metabolism is described. W. H. C. SHAW

2221. **The excretion of amino acids by the human. A quantitative study with ion-exchange chromatography. [Determination of β-amino*iso*butyric acid.]** D. F. Evered (Med. Unit, Univ. Coll. Hosp. Med. Sch., London). *Biochem. J.*, 1956, **62** (3), 416–427.—An ion-exchange method is described for the determination of β-amino*iso*butyric acid in urine. The results agree with those obtained by paper chromatography. A column (100 cm) of 4 per cent. cross-linked Dowex-50 resin is used, and the amino acids adsorbed from 1 to 5 ml of urine (previously adjusted to a pH of 4·3 to 4·5 by conc. HCl) are eluted with Na citrate buffer (pH 4·5). The first 70 ml of eluate are discarded and the β-amino*iso*-butyric acid is present at approx. 80 to 90 ml. Fractions of 1 ml each are collected and analysed by the colorimetric method in which ninhydrin - $SnCl_2$ is used, and the concn. of amino acid is ascertained by comparison with a calibration curve obtained with the pure acid. J. N. ASHLEY

2222. **Colorimetric determination of lysine with Folin's reagent.** Naokazu Sakota, Yoshimi Okada and Hiroko Urabe (Dainippon Zoki Inst., Higashisumiyoshi-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1046–1048.—The reaction (Nelson *et al.*, *Fed. Proc.*, 1946, **5**, 148) of brominated lysine with Folin's reagent (**I**) was applied to the determination of lysine in protein. Other amino acids, including tyrosine, phenylalanine and histidine, which interfere with the determination, can be separated by the use of Amberlite IRC-50(H). The sample soln. (hydrolysed protein, containing $\simeq$ 0·2 mg of lysine) is adjusted to pH 5·0 with a citrate buffer and passed through a column of Amberlite IRC-50 (diameter 1 cm, length 25 cm). The column is then eluted with 0·1 *M* citrate soln. (pH 5·0). The first 50-ml portion is rejected, then 5-ml portions are submitted to colorimetry until there is no reaction with **I**. A 2-ml portion of the eluate is treated with the buffer soln. (1 ml) and satd. bromine soln. (2 drops) in ice-cooled water for 20 min. The excess of Br is decomposed with Na_3AsO_3 (3 per cent. As_2O_3 in 1 per cent. NaOH) and heated at 60° C. The product is treated with Na_2CO_3 (20 per cent., 1·5 ml, at 60° C) and **I**, and the extinction of the cooled product is measured at 660 mμ after 30 min. K. SAITO

2223. **Identification of cystine with Folin's reagent.** Naokazu Sakota, Taneyoshi Yu, Yoshimi Okada and Sueo Suehiro (Dainippon Zoki Inst., Higashisumiyoshi-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (10), 1194.—It was found that Folin's phenol reagent (**I**) reacts with cystine soln. (in 0·01 *N* NaOH) in the presence of Cu to produce a distinctive blue colour. The extinction at 660 mμ obeys Beer's law for $<$ 0·6 mg of cystine per ml. Tyrosine, tryptophan and cysteine react with **I** in the absence of Cu; the reaction described is specific for cystine. K. SAITO

2224. **The detection of thyroxine and related compounds on paper chromatograms by optical methods.** N. F. Maclagan, C. H. Bowden and J. H. Wilkinson (Westminster Hosp., Med. Sch., London). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 633–636.—The ceric sulphate - arsenous acid reagent has been applied to the detection of thyroxine and tri-iodothyronine on paper chromatograms. The sensitivities achieved suggest that this reagent might enable physiological concn. of these substances to be detected. Preliminary experiments on the extraction of the iodine components of plasma are described. A procedure developed by Bowden and Maclagan (*Biochem J.*, 1954, **56**, vii) made it possible to detect 0·1 μg or even less of thyroxine or tri-iodothyronine; this is about 100 times the sensitivity to ninhydrin or diazotised sulphanilic acid. The chromatograms were stained yellow by the reagent and the positions of the iodo compounds appeared as white spots. Fat and protein must be removed by extraction with light petroleum and pptn. with methanol, respectively, before chromatography. P. HAAS

2225. **Estimation of amino nitrogen in synthetic polypeptides.** G. Kainz and F. Schöller. (Chem. Lab. Univ. Vienna). *Biochem. Z.*, 1955, **327** (4), 292–295.—Estimation of the terminal primary amino group of some simple synthetic di- and tri-peptides has been studied, the nitrous acid method being used. Possible secondary reactions of the peptides have been overcome to a great extent by the use of dilute $NaNO_2$ solution (1 or 5 per cent.) and 40 per cent. KI solution in the deamination process. G. W. CAMBRIDGE

2226. **Evaluation of paper electropherograms.** E. Krüger-Thiemer and W. Reif (Tuberkuloseforschinst., Borstel, Germany). *Klin. Wochschr.*, 1956, **34** (7–8), 205–207.—Two methods of calculating the percentages of all of the serum protein fractions are proposed for electropherograms that show no definite α_1-globulin peak. In the first procedure, perpendiculars are drawn from each of the four peaks given by albumin and α_2-, β- and γ-globulins so that the electrophoresis curve is divided into five areas, designated *A*, *B*, *C*, *D* and *E*, respectively, which are measured planimetrically or gravimetrically. If $F = A + B + C + D + E$, then the percentages of the fractions may be calculated as follows—albumin = $(2A/F)100$; α_1-globulin = $[(B - A - C + D - E)/F]100$; α_2-globulin = $[2(C - D + E)/F]100$; and γ-globulin = $(2E/F)100$. In the second procedure, perpendiculars are drawn from the albumin and α_2- and γ-globulin peaks only, and the half of the curve for α_2-globulin further from the albumin is drawn in so that five areas are obtained as before. Albumin and γ-globulin are then calculated as in the first procedure and α_1-globulin = $[(B - A - C)/F]100$; α_2-globulin = $(2C/F)100$; and β-globulin = $[(D - E)/F]100$. H. F. W. KIRKPATRICK

2227. **Micro-titration of proteins.** A. C. Maehly (Johnson Foundation, Univ. Pa., Philadelphia, U.S.A.). *Bull. Schweiz. Akad. Med. Wiss.*, 1955, **11** (6), 433–462.—The applicability of acid - base titration methods to proteins and the validity of the law of mass action for this type of titration is fully discussed; this is followed by an analysis of a number of experimental acid - base titration curves and the calculation of the most important sources of error and their avoidance. A new micro-method for protein titrations is described with illustrations; the method was used for titrating horse-radish peroxidase, and the results are compared with those obtained by Theorell with a conventional method. Quantitative determinations of ionisable groups are shown to be possible with as little as 2 mg of protein. P. HAAS

2228. **The separation and quantitative determination of the component sugars of mucoproteins.** A. Gottschalk and G. L. Ada (Walter and Eliza Hall Inst. of Med. Res., Melbourne, Australia). *Biochem. J.*, 1956, **62** (4), 681–686.—A method for the complete analysis of the sugar components of mucoproteins is described. The detrimental interaction between reducing sugars and amino acids is minimised by the use of a low temp. when high concn. of reactants are unavoidable and by removal of nitrogenous material before drying the sugars. The individual sugars are separated, identified, and determined by chromatographic methods. The accuracy of the method is within $\pm$ 10 per cent. The intrinsic sugars of a mucoprotein are recovered to an extent of 70 to 90 per cent. The degree of recovery is partly affected by the ratio of amino sugar to non-amino sugar; a low value favours a high recovery. J. N. ASHLEY

2229. **Plasma electrophoresis on filter-paper.** F. Scheifforth, G. Berg and H. Götz (Med. Univ. Klin., Erlangen, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 126–128.—After applying heparinised plasma to dry filter-paper, the paper is soaked in Michaelis buffer (pH 8·6) containing heparin (1:1000). Heparin need not be added to the buffer in the chamber, so simultaneous serum and plasma electrophoresis may be carried out. The fibrinogen appears between the β- and γ-globulins. Values giving reasonable agreement with the Tiselius method were found in 20 healthy persons. F. POWELL

2230. **Quantitative filter-paper electrophoresis of serum: automatic scanning and integration of the dye-stained strip.** I. R. Mackay (Sloan-Kettering Inst., New York, U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (1), 164–168.—The use of a commercially available (in U.S.) scanner and integrator for the examination of dye-stained paper-electrophoresis patterns of serum proteins is investigated. The instrument is found to be rapid and accurate and to give results that compare well with those obtained with a simple photometer and by free electrophoretic analysis. Normal values and standard deviations obtained by the use of the instrument are given. W. H. C. SHAW

2231. **Determination of serum-protein fractions by zone electrophoresis on paper and direct reflection photometry.** J. A. Owen (Dept. of Clin. Chem., Univ. Edinburgh, Great Britain). *Analyst*, 1956, **81**, 26–37.—The construction of a tank for zone electrophoresis on filter-paper is described and also a modification of the JLC reflectance densitometer. After electrophoresis of the protein sera the paper was dried and placed in a combined fixing and staining bath. The dyes fixed by the proteins were then eluted with suitable solvents and the extinctions of the eluates were measured spectrophotometrically. The reflection of light from the dyed protein fractions was also measured directly with the modified densitometer, and the results obtained by the two methods were compared. The adsorption of the dyes used was found to be approx. proportional to the protein concn. within certain limits. Normal and abnormal sera were examined by the two methods and the reproducibility of the results is indicated. Precision with elution is greater than with direct photometry. The validity of the results and of those obtained by other electrophoretic methods is discussed. A. O. JONES

2232. **The reliability of the electrophoresis on filter-paper of urinary proteins.** D. Wolvius (Univ. Hospital, Utrecht, Holland). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 596–602.—From an investigation of the paper electrophoresis of urinary proteins it is concluded that results are reliable only if the concn. is $\not<$ 2 per cent. P. HAAS

2233. **A method for protein-bound iodine: the kinetics and the use of controls in the ashing technique.** H. L. Thompson, M. R. Klugerman and J. Truemper (Second Army Area Med. Lab., Fort George G. Meade, Md., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (1), 149–163.—The sensitivity, accuracy and reproducibility of a modified dry-ashing (Na_2CO_3) technique for the determination of serum protein-bound iodine (**I**) have been investigated. Studies are made of the effects of various ions on the colorimetric assay of iodide by the ceric - arsenite method, of control methods to ensure max. accuracy by means of standard samples, of the kinetics of the ceric - arsenite reaction, and of the use of five different spectrophotometers and filter instruments for colour measurement. The normal range for **I** in serum is 3·5 to 8·0 μg per 100 ml with a mean of about 5·8 μg. W. H. C. SHAW

2234. **The determination of protein-bound iodine-131 with an anion-exchange resin column.** T. Fields, D. S. Kinnory, E. Kaplan, Y. T. Oester and E. N. Bowser (Veterans Admin. Hosp., Hines, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (2), 333–336.—In the method given, inorganic iodine is separated from the protein-bound iodine in 5 ml of heparinised plasma by passage through a narrow tube containing about 1·5 g of Amberlite resin IRA-400 previously converted to the chloride form by treatment with *N* NaCl and washed free from Cl′ with water. In studies with ^{131}I the eluate may be counted directly, but for comparison with results given by the trichloroacetic acid pptn. technique the eluate was pptd. similarly. Close agreement was found between results by the two methods in 100 consecutive thyroid-function studies.
W. H. C. SHAW

2235. **The differentiation of the serum lipoproteins by means of preparative electrophoresis.** F. Dietrich (Med. Univ. Klin., Marburg, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 227–235.—With potato starch as a supporting medium, 4 ml of serum are subjected to electrophoresis in Michaelis Na barbitone - Na acetate buffer (pH 8·6) at 4 V per cm for 20 hr. at 3° to 4° C. Dry filter-paper strips are then rolled over the starch block and the impressions obtained are stained with Amido black or bromophenol blue. The block is then divided into strips corresponding to the protein fractions or into strips 1 cm wide. The protein is then eluted with dilute buffer and the lipids are extracted in a Soxhlet apparatus for 6 hr. with ethanol and then for 1 hr. with ether. Cholesterol, phospholipid and esterified fatty acids are then estimated chemically in the extracts. Two lipid bands were found—one in the neighbourhood of the α_1-globulin having a cholesterol to phospholipid ratio of 0·53, and one with the β-globulin having a cholesterol to phospholipid ratio of 1·24. There is also a band with a weak peak near the α_2-globulin containing large quantities of fatty acids. The chylomicrons of neutral fat are also found here. In coronary infarction there was found to be a relative and absolute lowering of the α_2-lipoproteins with a corresponding increase in the β-band. The cholesterol to phospholipid ratio was, however, normal. F. POWELL

2236. **The separation of substances and estimation of their relative molecular sizes by the use of columns of starch in water.** G. H. Lathe and C. R. J. Ruthven (Queen Charlotte's Maternity Hosp., London, W.6). *Biochem. J.*, 1956, **62** (4), 665–674.—Neutral mol. are eluted from columns of potato starch in buffer in the descending order of their mol. wt. There is good resolution of substances in the mol.-wt. range of 100 to 1000. Large mol. remain outside untreated starch grains, but starch, swollen by warming in water, is permeable to larger mol., and in columns separates them in the range of mol. wt. 1300 to 15,000. Columns of starch in water are a new type of partition system in which the vol. of the stationary phase is determined for each substance by the depth to which it can penetrate the starch granules. The possibility of determination of mol. wt. with these columns is discussed. J. N. ASHLEY

2237. **Recent work on the determination and identification of 17-ketosteroids and corticosteroids.** R. Henry (l'Hôpital, Tenon, France). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 442—466.—The separation of 17-ketosteroids and of corticosteroids can be effected by chromatography, with either a column of alumina or with paper. The eluted products are characterised by colour reactions or i.r. or u.v. spectrophotometry. Some data are given for a few of the steroids that occur in serum.
P. HAAS

2238. **The polarographic estimation of ketosteroids.** C. J. O. R. Morris (The London Hospital, Whitechapel, London). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 476–497.—The technique of the determination of ketosteroids by polarography of their Girard hydrazones is discussed, with special reference to the determination of 17- and Δ^4-3-ketosteroids. Application of the polarographic method to the determination of urinary 17-ketosteroids is described, together with a new rapid procedure in which the hydrolysis of the steroid complexes with toluene-*p*-sulphonic acid is employed. The use of polarography in the determination of individual corticosteroids in human blood is demonstrated and experimental procedures and results are given. P. HAAS

2239. **The combined application of Craig distribution and paper electrophoresis for the separation of steroid mixtures.** W. Schröder, K. P. Voigt and I. Beckmann (Lab. der 2 med. Klin. der Univ., Hamburg, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (2–3), 63–67.—Testosterone (**I**), deoxycorticosterone (**II**), cortisone (**III**) and 17-hydroxycorticosterone (**IV**) can be separated by paper electrophoresis with a current of 400 V for 2 to 4 hr. after esterification with succinic acid. The position of the steroids can be detected by observing the colour developed with 15 per cent. H_3PO_4 or 10 per cent. NaOH in u.v. light. **II** and **IV** travel the farthest, but both travel the same distance; the fluorescence colours are rose and yellow, respectively. **III** travels rather less and fluoresces blue, whereas **I** travels least and fluoresces orange. Craig distribution in an apparatus with 33 steps in a quaternary-phase system, of which the lower layer is composed of equal parts of $CHCl_3$ and CCl_4 and the upper layer equal parts of methanol and phosphate buffer pH 6·8, also gave satisfactory separation. The partition curve was determined by measuring the extinction at 245 mμ. The order of separation was **IV**, **III**, **II** and **I**. F. POWELL

2240. **Use of ^{131}I-labelled substrates in the determination of proteolytic and lipolytic enzymes.** G. Brante (Centrallasarettet, Eskilstuna, Sweden). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 370–372.—When ^{131}I-labelled protein or fat is used as substrate for proteolytic or lipolytic enzymes, respectively, unsplit substrate as well as split products can be readily evaluated quant. by measurement of their radioactivity. P. HAAS

2241. **The determination of the cholinesterase activity of the blood for the detection of poisoning by organophosphorus insecticides.** J. Fournel (Usines Chimiques Rhône-Poulenc, Vitry S/Seine, France). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 640–645.—The measurement of the cholinesterase activity of the blood of persons in contact with organophosphorus insecticides provides a means of detecting any accidental absorption of these substances before the appearance of subjective symptoms. For the measurement of the activity, blood is taken by venous puncture from a

fasting patient and defibrinated by beating. The washing of the corpuscles and prep. of their haemolysates and dilution of the serum are carried out according to Michel's method (*J. Lab. Clin. Med.*, 1949, **34**, 1564). The soln., 0·5 ml, corresponding to 0·1 ml of serum or 0·05 ml of red blood corpuscles, is equilibrated at 38° C in a Warburg apparatus then mixed with 2·5 ml of a 0·16 *M* soln. of acetylcholine hydrochloride containing 0·2 per cent. of $NaHCO_3$; readings of the CO_2 evolved are taken every 10 min. for 30 min. The activity of the acetylcholine is expressed by the number of μl of CO_2 evolved in 30 min. by the enzyme contained in 0·1 ml of serum or 0·05 ml of red blood corpuscles. The mean values of the cholinesterase activity of 60 persons who had never been exposed to the poison were found to be 235 $\pm$ 53 and 118 $\pm$ 15 for serum and red blood corpuscles, respectively. P. HAAS

2242. **Self-equilibrating electrolytic method for determination of acid production rates [by cholinesterase].** D. W. Einsel, jun., H. J. Trurnit, S. D. Silver and E. C. Steiner (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 408–410.—An automatic electrolytic titrator is described for measuring cholinesterase activity, quickly and accurately. The titrator is designed to measure directly the rates of acid-producing reactions but, with modifications, it may be applied to other types of reaction. The standard deviation of measurements of rate of acid production on 10 portions of a sample was $\pm$ 0·04 micro-equivalent per min. G. P. COOK

2243. **The significance of routine phosphatase determinations in clinical laboratories.** S. Raabe (Univ. Clinic, Freiburgi Br., Germany). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 652–660.—A detailed description is given of methods for determining total P, and alkaline and acid phosphatases. It is claimed that these methods give accurate results and are simple enough to be carried out in large numbers. P. HAAS

2244. **The comparison of results obtained by various methods for the determination of diastase in blood.** K. Heinkel (Erlangen Univ., Germany). *Klin. Wochschr.*, 1956, **34** (5–6), 155–157.—The results obtained for the diastase content of serum by various methods are comparable only when the basic principles of the determination are similar. It is thought that the differences are due to the presence of α- and β-amylases. P. S. STROSS

2245. **Determination of cocarboxylase in blood.** W. W. Kay and K. C. Murfitt (West Park Hosp., Epsom, Surrey). *Biochem. J.*, 1956, **62** (4), 601–605.—The cocarboxylase in heated blood cells is recombined with apocarboxylase prepared from yeast; the resulting haloenzyme is used in the decarboxylation of pyruvic acid, and the CO_2 evolved is determined manometrically. Norit is used to remove cocarboxylase during the preparation of the apoenzyme from yeast. Cyanide or thiosulphate is added to the enzyme system to eliminate the effects of interfering substances, probably trace metals; and an internal standard ensures identical conditions of activation in the tests and standards. Over the range of 0 to 0·2 μg of cocarboxylase there is a linear relationship between CO_2 and cocarboxylase. J. N. ASHLEY

2246. **Studies in histochemistry. XXXVIII. Determination of succinic dehydrogenase in microgram amounts of tissue and its distribution in rat adrenal.** C. D. Jardetzky and D. Glick (Dept. of Physiol. Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *J. Biol. Chem.*, 1956, **218** (1), 283–292.—The colorimetric method described is based on the use of neotetrazolium chloride as the hydrogen acceptor. The precision and sensitivity of the method are increased by the use of a mixture of alcohol and tetrachloroethylene for extraction of the formazan product and the use of EDTA (disodium salt) as an activator of the enzyme. The formazan is determined colorimetrically at 519 mμ and the amount is ascertained by comparison with standard solutions. The error is within $\pm$ 5 per cent. J. N. ASHLEY

2247. **Micro-determination of α-keto acids with special reference to malic, lactic and glutamic dehydrogenases in brain.** E. Robins, N. R. Roberts, K. M. Eydt, O. H. Lowry and D. E. Smith (Washington Univ. Sch. of Med., St. Louis, Mo., U.S.A.). *J. Biol. Chem.*, 1956, **218** (2), 897–909.—A sensitive, colorimetric micro-method is described for the determination of as little as 4×10^{-10} mole of an α-keto acid. The acid is converted into its 3-quinolylhydrazone, and the extinction of the resulting solution is determined at 305 mμ. Since malic, lactic and glutamic dehydrogenases convert their respective substrates into keto acids, the method can be used for the determination of these enzymes in 0·05, 0·1 and 0·5 μg dry wt. of brain, respectively. α-Keto acids can be determined in the presence of ketones, β-keto acids, and aldehydes because the 3-quinolylhydrazones obtained from these compounds are unstable and have different u.v. spectra from those obtained with α-keto acids. J. N. ASHLEY

2248. **Colorimetric estimation of arylsulphatase: enzyme kinetics and distribution of the enzyme in seven mammals and in tumours.** A. M. Rutenburg and A. M. Seligman (Harvard Med. Sch., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **60** (1), 194–214.—In the method described, potassium 6-benzoyl-2-naphthyl sulphate (substrate) is incubated at pH 6·1 with a homogenate of the tissue under test. The azo dye formed on the addition of tetrazotised *o*-dianisidine to the incubated mixture is extracted into chloroform and determined photo-electrically. The effect of pH, temp., incubation time and concn. of tissue and substrate on the rate of the enzymatic hydrolysis of the substrate is studied in detail, and the method is applied to the determination of arylsulphatase activity in various human and other mammalian tissues. W. H. C SHAW

2249. **The determination of triosephosphatase isomerase.** W. S. Beck (Univ. Calif. Med. Center, Los Angeles, Calif., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **60** (1), 1–6.—The method described is based on the different rates of reaction of 2:4-dinitrophenylhydrazine with glyceraldehyde 3-phosphate (**I**) and dihydroxyacetone phosphate (**II**), the equilibrium between which is catalysed by triosephosphate isomerase. The sample is added to a buffered system containing **I**, the mixture is incubated at 38° C for exactly 10 min., excess of NaOH is added and the colour is measured at 550 mμ. From the ratio of **I** to **II**, calculated by the method given, and the total alkali-labile

phosphorus, detd. separately, the rate of conversion of **I** into **II** and hence the isomerase activity can be calculated. W. H. C. SHAW

See also Abstracts 1962, 1973, 1974, 1985, 2043, 2122, 2132, 2272, 2309, 2314, 2377.

Drugs

2250. **A note on the determination of codeine in aspirin, phenacetin and caffeine with codeine tablets.** M. Pernarowski (Dept. Nat. Health and Welfare, Ottawa, Ontario, Canada). *Drug Standards*, 1955, **23** (5), 157–158.—Chlorophenol red (2 drops of a 0·5 per cent. soln. in 8 per cent. w/v phenol in $CHCl_3$) may be used as an indicator in the non-aq. titration of codeine phosphate (*cf. Anal. Abstr.*, 1955, **2**, 1324) with 0·05 *N* $HClO_4$ in dioxan. The end-point is marked by a colour change from pale yellow to colourless, and coincides with the potentiometric end-point (although potentiometric titration requires the use of the stabilising solvent methyl cyanide). A. R. ROGERS

2251. **A modified colorimetric assay for belladonna alkaloids.** W. Saski (Coll. of Pharmacy, Univ. Nebraska, Lincoln, Nebr., U.S.A.). *Drug Standards*, 1955, **23** (5), 149–153.—A colorimetric assay is given for total alkaloids in belladonna leaf. It involves complex-formation with Cu^{++} and oleic acid (*cf. J. Amer. Pharm. Ass., Sci. Ed.*, 1953, **42**, 361). The results are comparable with those obtained by the U.S.P. XIV method. *Procedure*—Extract the sample (10 g) by the U.S.P. method. After the last 15-min. heating of the purified alkaloids, dissolve the residue in the minimum volume of $CHCl_3$ and dilute with benzene to 50 ml. To a 25-ml aliquot, add a freshly prepared 10 per cent. soln. of oleic acid in benzene (2 ml) and a 5 per cent. aq. soln. of $Cu(NO_3)_2$ (2 ml) and dilute with benzene to 50 ml. Prepare a control soln. similarly from the other 25-ml aliquot, but with water in place of Cu^{++} solution. After 24 hr., compare the extinctions at 710 mμ, and calculate by use of a standard atropine curve. A. R. ROGERS

2252. **Assay of strychnine in nux vomica, St. Ignatius beans and galenical preparations.** M. Carlassare (Lab. della propria Farmacia, Vicenza). *Il Farmaco, Pract. Ed.*, 1955, **10** (12), 662–669.—The alteration in the strength of the acid used for the oxidation of brucine in the International Pharmacopoeia from that used in the B.P. causes the loss of strychnine to be negligible. The correction applied (by the use of the same factor as in the B.P. method) is unnecessary. N. E.

2253. **The determination of *iso*lysergic hydrazide with 0.05 *N* perchloric acid in an acetic acid - acetic anhydride medium.** I. Gyenes (Pharmaceutical Factory of Kőbánya, Budapest.) *Magyar Kém. Foly.*, 1956, **62** (1), 26–27.—Dissolve the *iso*lysergic hydrazide (**I**) (60 to 200 mg, dried over P_2O_5) in acetic acid (20 ml) containing 15 per cent. v/v of acetic anhydride, in a flask with a ground glass stopper, while protecting it from light. After 10 min., add 1 drop of 10 per cent. crystal violet in acetic acid and titrate with 0·05 *N* $HClO_4$ to a blue colour (first colour change). The $HClO_4$ soln. is standardised against *sym.*-diphenylguanidine in acetic acid. A blank for the solvent and indicator has to be determined. The error of a single determination is ± 0·3 per cent. A. G. PETO

2254. **Titration of drugs and chemicals in non-aqueous solutions. V. Determination of methylxanthines in glacial acetic acid.** Tetsu Kashima (National Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (10), 1078–1080.—Theophylline, theobromine and caffeine can be potentiometrically titrated in glacial acetic acid (**I**) (0·02 to 0·01 *N*) with $HClO_4$ by the use of a glass electrode and a S.C.E. as reference electrode. The titration can also be carried out by adding a known amount of $HClO_4$ and titrating the excess with K_2CO_3, K H phthalate, Na_2CO_3 or pyridine (0·1 *N* in **I**), with crystal violet, malachite green or methyl violet (0·5 per cent. in **I**) as indicator. A mixture of caffeine and sodium salicylate or benzoate is differentially titrated with slightly less accuracy, the first stage corresponding to the neutralisation of the sodium salt and the second to that of the caffeine. K. SAITO

2255. **Studies on digitalis. II. Paper partition chromatography of *Digitalis purpurea* glycosides.** Yoshio Sasakawa (Res. Lab., Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (7), 721–723.—A mixture of glycosides in *Digitalis purpurea* can be separated by paper chromatography into two groups, having R_F values < 0·1 (true glycosides) (**I**) and > 0·6 (digitoxin class and genin group) (**II**), by the use of a mixture of chloroform, ethanol and water (10 + 2 + 10). The filter-paper is cut into two and both parts are separately extracted with a mixture of chloroform and ethanol (2 + 1), the extracts are evaporated *in vacuo* and submitted to further partition chromatography. When **I** is developed with a mixture of ethyl acetate, benzene, ethanol and water (84 + 14 + 20 + 50), the R_F values are—digitalinum verum, 0·18; purpurea glycoside B, 0·39; purpurea glycoside A, 0·59. When **II** is developed with a mixture of benzene, ethyl acetate and water (2 + 1 + 1), the R_F values are—gitoxin, 0·05; digitoxin, 0·36; gitoxigenin, 0·55; digitoxigenin, 0·81. The spots are detected with trichloroacetic acid (25 per cent. in chloroform) or $SbCl_3$ (20 per cent. in chloroform). K. SAITO

2256. **Anthraquinones and anthraquinone glycosides. An approximately quantitative assay of genuine reduced glucofrangulin derivatives in acetylated fractions of extract of *Rhamnus frangula* bark.** H. Mühlemann (Pharm. Inst. Univ. Bern, Switzerland). *Pharm. Acta Helv.*, 1955, **30** (9), 350–355.—The content of glucofrangulin anthranol acetate (**I**) of acetylated extracts of Cortex Rhamni Frangulae can be followed by a spectrophotometric method. The extinction at the maximum at 395 mμ and the minimum at about 320 mμ of successive fractions is measured and the quantity present estimated from the difference of these two values. $E^{1\%}_{1\,cm}$ (max.) at 395 mμ $- E^{1\%}_{1\,cm}$ (min.) at about 320 mμ ≃ 65. Pure **I** was obtained, but could not be crystallised. P. S. STROSS

2257. **Hydroxyanthrones in plants containing hydroxyanthraquinones. VII. A new method for the micro-determination of 1:8-dihydroxyanthrone derivatives and the seasonal variance of their content in plants.** Kiyoshi Tsukida and Nobuo Suzuki (Kobe Women's College of Pharm., Motoyama-cho, Higashinada-ku, Kobe). *J. Pharm. Soc. Japan*, 1954, **74** (10), 1092–1096.—The determination of 1:8-dihydroxyanthrones [chrysophanic acid anthrone (**I**), emodin anthrone (**II**) and rhein anthrone

(**III**)] in anthrone-containing plants was studied by the use of dimethyl-*p*-nitrosoaniline (**IV**) (0·1 per cent.) in pyridine. The corresponding hydroxyanthraquinone derivatives (*i.e.*, chrysophanic acid, emodin and rhein) fail to give similar reactions with **IV**; they react with Mg acetate in pyridine to give a reddish colour. **I**, **II** and **III** can be separated by paper chromatography with *cyclo*hexane saturated with methanol, each spot overlapping that of the corresponding anthraquinone derivative. The spots are extracted with pyridine and determined colorimetrically. The extinction of the resulting soln. (**I**, 620; **II**, 605; **III**, 660 mμ) is proportional to the concn. for 5 to 25 μg of each per ml. Hydroxyanthraquinones, flavonoids and sugars do not interfere. K. Saito

2258. **Capsicum. I. Colorimetric determination of capsaicin by paper partition chromatography.** Mitiiti Fujita, Tsutomu Furuya and Akira Kawana (Dept. of Pharm., Medical Faculty, Tokyo Univ., Hongo). *J. Pharm. Soc. Japan*, 1954, **74** (7), 766–770.—Büchi's method (*Pharm. Acta Helv.*, 1948, **23**, 327, 353) for the chromatographic determination of capsaicin (**I**) was modified for use in the determination of **I** in capsicum and its tincture. The sample (5 g) is extracted with acetone (30 ml), filtered and made up to 50 ml. A 1-ml portion is evaporated and extracted with ethanol; two portions of the ethanolic extract are chromatographed and developed with benzene saturated with methanol for 3·5 to 4·0 hr. The **I** on one of the papers is revealed with 0·1 *N* NaOH and 3 per cent. molybdophosphoric acid (**II**); the corresponding spot of **I** on the other paper is cut out, extracted with methanol (30 ml) for 1 hr., and the extract is evaporated to dryness. The residue is dissolved in 0·1 *N* NaOH (5 ml), treated with **II** (3 ml) and the extinction measured at 730 mμ. K. Saito

2259. **Colorimetric determination of ascaridole with the Beckman spectrophotometer.** Kazutaka Yamaguchi and Hatsue Shoji (National Hygienic Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (8), 846–849.—Ascaridole (**I**) oxidises quinol in ethanolic soln. in the presence of HCl. When the resulting brown colour is measured at 400 or 420 mμ, the extinction - concn. diagram is linear within the range 50 to 500 mg of **I** in 100 ml. Low-boiling fractions of chenopodium oil fail to show a similar coloration. The standard deviation is about $\pm$ 0·0217 (400 mμ). The results are intermediate between those by the iodimetric method and Nelson's method. An ethanolic soln. of the sample (5 ml) is treated with quinol (5 per cent. in ethanol) (2 ml) and conc. HCl (1 ml) at 70° C for 20 min., and submitted to spectrophotometry. K. Saito

2260. **Applications of nitrometry. VIII. Determination of folic acid.** Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (12), 1310–1311.—Folic acid is reduced in an HCl soln. with Zn to give 2-amino-4-hydroxy-6-methylpteridine and glutamyl *p*-aminobenzoic acid; the acid can be determined by nitrometer, with the use of NaN_3. The sample (40 to 160 mg) is dissolved in 6 *N* HCl (40 ml) and made up to 100 ml with water. A 15 to 20-ml portion is shaken with zinc dust (0·5 g) for 15 min. and filtered. An aliquot (1 ml) of the filtrate is treated with a cold soln. of 6 *N* HCl (0·1 ml) and KNO_2 (0·4 per cent., 1 ml) for 2 min., then with ammonium sulphamate (0·4 per cent. in 25 per cent. acetic acid, 0·1 ml) and submitted to nitrometry, as described in Part VII (*cf. Anal. Abstr.*, 1956, **3**, 2149). K. Saito

2261. **Chromatographic determination of insulin potency.** Takeshi Asaoka and Katsumi Higashi (Taiyo Fisheries Co., Nishi-12, Tsukishima, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (7), 788–790.—Robinson's method for the determination of insulin in protamine zinc insulin (*Biochem. J.*, 1952, **51**, 298) was applied to the determination of the purity of crude insulin. On the chromatogram of insulin, obtained by Robinson's method, a band is observed at a point R_F 0·40, which appears to arise from an insulin-like substance without potency. The sample (5 mg) is dissolved in 2 per cent. acetic acid to produce a 1 per cent. soln. A 0·15-ml portion is spotted on a filter-paper, developed with a mixture of glacial acetic acid, butanol and water (1 + 3 + 4), and revealed with bromocresol green. The two bands of R_F 0·45 and 0·40 are clearly separated; they are cut out, extracted with a buffer soln. (pH 9·2) and submitted to spectrophotometry (620 mμ). K. Saito

2262. **Countercurrent distribution of the tetracycline antibiotics.** A. G. Mistretta and P. P. Minieri (American Cyanamid Co., Princeton, N.J., U.S.A.). *Antibiot. & Chemother.*, 1956, **6** (1), 13–18.—The method described is suitable for the determination of tetracycline, chlortetracycline and oxytetracycline in 5-mg samples of mixtures of the three antibiotics. A 10-ml, 50-tube glass countercurrent apparatus is used, and distribution is between chloroform and aq. buffer (pH 4·5), prepared by mixing 0·2 *M* sodium phosphate and 2·25 per cent. citric acid. After equilibration, 4 ml of the aq. phase from each tube are diluted with 1 ml of 0·5 *N* H_2SO_4 and the extinction is measured at 265 mμ. Separation of the three antibiotics is not complete, but is sufficient for the composition of the sample to be calculated by the method given. W. H. C. Shaw

2263. **A sensitive plate-assay for polymyxin in pharmaceutical preparations, serum and other body fluids.** B. Arret and A. Kirshbaum (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1956, **6** (2), 95–99.—The sensitivity of the FDA plate-assay for polymyxin with *Brucella bronchoseptica* is increased by changing the concn. of phosphate buffer, pH 6·0, from 1 to 10 per cent. Test solutions prepared from samples of polymyxin or from pharmaceutical preparations can be assayed at concentrations of 6 to 15 units per ml, dilutions at which the proportions of neomycin, sulphonamides, sodium ethylmercurithiosalicylate or sucrose which may be present in polymyxin preparations do not interfere. By mixing equal parts of 20 per cent. phosphate buffer (pH 6·0) and human serum or 7 per cent. bovine albumin in 0·1 *M* phosphate buffer (pH 7·4), serum concentrations of polymyxin down to 0·5 unit per ml can be detected. W. H. C. Shaw

2264. **Streptonivicin [Novobiocin], a new antibiotic. II. Isolation and characterisation.** H. Hoeksema, M. E. Bergy, W. G. Jackson, J. W. Shell, J. W. Hinman, A. E. Fonken, G. A. Boyack, E. L. Caron, J. H. Ford, W. H. Devries and G. F.

Crum (Upjohn Co., Kalamazoo, Mich., U.S.A.). *Antibiot. & Chemother.*, 1956, **6** (2), 143–148.—Details are given of the behaviour of streptonivicin (**I**) in countercurrent distribution analysis, of its u.v. absorption spectra at different pH values, the melting points and infra-red absorption spectra of two crystalline forms of **I**, optical rotation, X-ray crystallographic analysis and paper chromatography in four solvent systems. Information is also given on the sodium and calcium, acid and dibasic salts of **I**.

III. *In vitro* and *in vivo* evaluation. J. R. Wilkins, C. Lewis and A. R. Barbiers. *Ibid.*, 1956, **6** (2), 149–156.—The sensitivities of 72 strains of micro-organisms to **I**, the influence of induced resistance to other antibiotics on sensitivity towards **I** and the sensitivity of **I**-resistant strains to other antibiotics are studied.

IV. A biological assay for body tissues and fluids. R. M. Taylor, W. T. Sokolski, G. M. Savage and M. J. Vander Brook. *Ibid.*, 1956, **6** (2), 157–161.—A simple serial-dilution method with *Micrococcus aureus* (ATCC 6538P) as test organism is found satisfactory for determining concn. of **I** above 8·0 μg per ml in serum, and will detect smaller concn. in urine. The sensitivity of the method may be increased to determine levels down to 0·5 μg per ml in urine, milk, human cerebrospinal fluid and homogenates of dog tissues by diluting the sample with 1 vol. of water, adjusting to pH 4 with *N* HCl and extracting with 2 vol. of ethyl acetate. The residue obtained by evaporating an aliquot of the solvent is dissolved in saline phosphate buffer and assayed by the method given.

W. H. C. Shaw

2265. **The micro-estimation of barbiturates. A new micro-technique.** E. Pfeil and H. J. Goldbach (Inst. für gericht. u. soziale Med., Univ. Marburg, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (4–6), 263–267.—The barbiturate is pptd. with Hg and the Hg is estimated colorimetrically by means of dithizone. Since 0·1 μg of Hg can be determined, similar quantities of barbiturate should be capable of estimation. The method is suitable for estimating barbiturate concn. on paper chromatograms and can be applied when other reagents have been used to locate the barbiturate spots, but even when chromatograms have not been run, the reaction is carried out on filter-paper. The mercury compound of hexobarbitone is too soluble for reliable results, but other barbiturates should be satisfactory. The method has been tested for cyclobarbitone, barbitone and phenobarbitone. There is a linear relationship between mercury dithizonate colour and barbiturate concn. over the range 1 to 70 μg. The whole procedure must be carried out rapidly. *Procedure*—The barbiturate soln. is spotted on to the middle of a piece of filter-paper (Schleicher and Schüll 2043*b*) and treated with 0·5 ml of reagent [500 ml of 1 per cent. $Hg(NO_3)_2$ + 10 ml of methanol], which is applied from a dropping pipette to the outer edge of the barbiturate spot. The paper is then placed in a Büchner funnel and suction applied. A device for giving instant control of suction while leaving the operator's hands free is described. The spot is washed with 0·5 ml of 0·5 *N* H_2SO_4 and the paper is placed in a separating funnel. Two per cent. HCl (5 ml), 6 *N* acetic acid (5 ml) and *N* H_2SO_4 (20 ml) are then added, followed by 20 ml (accurately measured) of a freshly made dithizone soln. (3 mg per 250 ml of $CHCl_3$). The mixture is shaken, the organic layer is removed and its extinction is determined at 610 mμ. It is essential to carry out a paper blank on the paper alone.

F. Powell

2266. **The separation of phenobarbitone and diphenylhydantoin by paper chromatography.** A. S. Curry (Home Office Forensic Sci. Lab., 32 Rutland Drive, Harrogate, Yorks., England). *Analyst*, 1955, **80**, 902–903.—Difficulties occur in the separation of sodium diphenylhydantoin (phenytoin sodium B.P.) and phenobarbitone in toxicological work. Both are extracted from protein-free aq. extracts by organic solvents at pH 3, both give the cobaltammine reaction, and diphenylhydantoin interferes with the spectrophotometric determination of phenobarbitone at 240 mμ. The drugs can be separated by paper chromatography and a visual comparison of the amounts present is possible. With the upper layer of the solvent system *n*-butanol - water - aq. NH_3 (100:66:33) and Whatman No. 1 paper, phenobarbitone has an R_F value of 0·50 and diphenylhydantoin of 0·65. To detect the compounds two methods are used. In the first, the dried chromatogram is contact-printed on photographic paper in u.v. light. The compounds absorbing u.v. light appear as white spots on the black background of the developed paper. The other, a colorimetric method, is a modification of that of Algeri *et al.* (*Brit. Abstr. C*, 1952, 349) in which the paper is treated with a soln. of HgO in H_2SO_4, washed with water, acetone and alcohol and finally with ethanolic diphenylcarbazone. The first method detects 10 μg of phenobarbitone or 20 μg of diphenylhydantoin and is about twice as sensitive as the second. The effect of the presence of other barbiturates is discussed.

A. O. Jones

2267. **Note on chromatographic assay of aspirin, phenacetin and caffeine tablets.** S. W. Goldstein and D. P. Sanders (Amer. Pharm. Ass., Washington, D.C., U.S.A.). *Drug Standards*, 1955, **23** (5), 180.—For the assay of tablets of aspirin (**I**), phenacetin (**II**) and caffeine (**III**), the A.O.A.C. method may be used to separate **I**, and the chromatographic method of Banes (*cf. Anal. Abstr.*, 1955, **2**, 435) to separate **II** and **III**. If emulsions form in the extraction of **I**, filter the $CHCl_3$ suspension through a layer of Dicalite 4200.

A. R. Rogers

2268. **Colorimetric determination of *p*-acetophenetidide [phenacetin].** F. J. Bandelin and R. E. Pankratz (Eaton and Co., Decatur, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 218–221.—The method is based on the hydrolysis of phenacetin with H_2SO_4 to *p*-phenetidine, which is diazotised and coupled with 2-naphthol in alkaline soln. The extinction is then measured. The mean recovery was 99·87 per cent. with a standard deviation of $\pm$ 0·28 per cent. and as little as 5 μg can be determined. The method was successfully applied to the assay of tablets and capsules.

G. P. Cook

2269. **Microchemical identification of local anaesthetic drugs.** E. G. C. Clarke (Royal Vet. Coll., London, England). *J. Pharm. Pharmacol.*, 1955, **8** (3), 202–206.—Tests are described for the identification of microgram quantities of 21 local anaesthetic drugs; crystal formation with alkaloidal reagents (*cf. Anal. Abstr.*, 1955, **2**, 2201) and colour reactions (diazotisation and coupling with 2-naphthol; *p*-dimethylaminobenzaldehyde; Vitali's test) are used.

A. R. Rogers

2270. **The paper chromatography and paper electrophoresis of local anaesthetics of the procaine series and their decomposition products.** G. Wagner and U. Zimmer (Pharm.-chem. Inst., Univ. Greifswald, Germany). *Pharm. Acta Helv.*, 1955, **30** (10–11), 385–407.—Some of the local anaesthetics based on procaine can be separated for identification by ascending paper chromatography by the use of mixtures of *n*-butanol, water and HCl. Spots are detected by Dragendorff's reagent; in addition, free amines can be diazotised and coupled. A list of R_F values of 13 anaesthetics in this group is given. Better separation is obtained on paper buffered with citrate (pH 2 to 4) and phosphate (pH 5 to 8) buffers with water-saturated butanol as solvent. Hydroxyprocaine - procaine and chloroprocaine - Tutocaine are not completely separated by either method, but are distinguished by colour reactions or by hydrolysis and chromatographic identification of the products on buffered paper. Electrophoresis (210 V) does not separate the anaesthetics from each other, but separates them from their hydrolysis products. P. S. Stross

2271. **Detection of some nerve stimulants [sympathomimetics].** Kakuma Nagasawa and Seiichi Ohkuma (National Hygienic Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (7), 773–778.—The detection of methylamphetamine (**I**) and amphetamine (**II**) in a mixture with ephedrine (**III**) was studied on a micro scale. The sensitivity of Waschmuth's method for the detection of **III** with ninhydrin (*J. Pharm. Belg.*, 1949, **4**, 186) is markedly increased by the use of pyridine in place of Na_2CO_3 (limit of detection, 3 μg); **I** and **II** do not interfere. **I** is oxidised with a mixture of $K_3Fe(CN)_6$, $Na_2[Fe(CN)_5NO]$ (**IV**) (both 5 per cent.) and Na_2CO_3 (2 *N*) at 80° C (60 to 90 sec.) and the product (formaldehyde) is detected with HCl and phenylhydrazine (red coloration). Other amines, including **II**, **III** and aromatic amines, fail to show similar reactions. **II** is treated with **IV** (5 per cent.), acetone (1 drop) and a small amount of $NaHCO_3$ soln. (pH 9·4 to 9·6) at 60° C (30 sec.) and yields a violet to purple colour. **I** and **III** give a pale-orange colour under the given conditions. K. Saito

2272. **Spectrophotometric determination of 3:3-diethyl-1:2:3:4-tetrahydro-2:4-dioxopyridine.** O. Pribilla (Inst. gericht. u. sozial. Med., Univ. Kiel, Germany). *Arzneimittel-Forsch.*, 1956, **3** (3), 138–142.—3:3-Diethyl-1:2:3:4-tetrahydro-2:4-dioxopyridine ("Persedon") (**I**) shows an absorption max. at 296 mμ in $CHCl_3$ soln., with $\epsilon = 9557$. In water, pH affects the u.v. absorption; the max. is displaced to 360 mμ in alkaline soln., owing to keto - enol tautomerism, and values of the equilibrium constant at various pH values are tabulated. The absorption max. in $CHCl_3$ may be used for the determination of **I** in tablets, urine, blood and organs; the assays usually involve extraction with $CHCl_3$ of an aq. soln. at pH 6. A. R. Rogers

2273. **Absorption spectrophotometry in the study of medicinal sulphur-containing preparations. Its use in ultra-violet, visible and infra-red analysis.** B. Salvesen. *Medd. Norsk Farm. Selsk.*, 1955, **17** (12), 365–372.—Having found that metallic Cu, anhydrous $CuSO_4$ and CuO induce the catalytic decomposition of org. compounds of S containing the grouping –NH·CS·NH– or NH·CS·S–, the author has developed a method for the determination of a number of compounds used in pharmacy such as thiourea, allylthiourea and derivatives of thiouracil and thiohydantoin. Soln. of these substances in *iso*propyl alcohol or *cyclo*hexane treated with Cu turnings undergo a change in their absorption curve. Disulfiram dissolved in *iso*propyl alcohol in contact with Cu turnings rapidly produces a yellow compound having an absorption max. at 434 mμ. Standard curves for disulfiram in acetone have been constructed for soln. of about 1 mg per 100 ml and successive quant. Ten ml of each soln. are treated with 0·45 g $\pm$ 5 mg of Cu turnings, previously washed with HNO_3, water, ethanol and ether. The max. colour is produced in 7 hr. and is stable for 0·5 to 1 hr. The method can be used for determinations in the presence of other substances which do not react with Cu. Thiourea breaks up giving compounds which do not absorb in u.v. and consequently phenothiazine can be determined in admixture with this substance. P. Haas

2274. **Photometric determination of 2:4-diamino-5-phenylthiazole [amiphenazole].** P. Lundgren (Apotekens Kontrollab., Stockholm, Sweden). *J. Pharm. Pharmacol.*, 1956, **8** (3), 185–190.—The method described for the determination of amiphenazole hydrochloride (**I**) or hydrobromide in aq. soln. is based on pptn. as the insol. reineckate. 2-Amino-4-hydroxy-5-phenylthiazole, 2-ethyl-2-methylglutarimide and moderate amounts of glycerol and ethanol or of benzyl alcohol and propane-1:2-diol do not interfere; poly(ethylene glycol) must be absent. *Procedure*—Cool the soln. (2 to 15 ml, containing 15 to 30 mg of **I**) in an ice-bath. Add a satd. soln. of ammonium reineckate, mix and allow to stand in the ice-bath for 15 min. Filter through a G4 sintered-glass crucible, wash the ppt. twice with iced water (2 ml) and dry by suction. Dissolve the ppt. in acetone, dilute to 25 ml, and measure the extinction at 525 mμ against water in 1-cm cells. Beer's law is obeyed over the concn. range 0 to 1·4 mg per ml. A. R. Rogers

2275. **Applications of nitrometry. VI. Determination of sulphonamides.** Masaharu Yamagishi and Makoto Yokoo (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (9), 961–962.—Sulphonamides react with an acidic soln. of KNO_2 to give a stable diazonium compound. After the decomposition of the excess of NO_2', the product is submitted to nitrometry, with the use of NaN_3. The sample (4×10^{-6} to 5×10^{-7} mole per ml) is treated with HCl (20 per cent., 0·3 ml) and KNO_2 (0·04 per cent., 1 ml) at 0° to 3° C for 2 min. The product is treated with ammonium sulphamate (4 per cent. in 25 per cent. acetic acid) (0·5 ml) and the N is removed. The soln. is introduced into a nitrometer and CO_2 is bubbled through. A soln. of NaN_3 (2 per cent. in water saturated with $NaNO_3$ and CO_2) is added to the nitrometer, which is shaken for 2 min. Sodium hydroxide (40 per cent.) (1·5 ml) is then introduced to absorb the CO_2, and the volume of N, which is equiv. to the sulphonamide, is measured. K. Saito

2276. **Titration of sulphonamides in non-aqueous solvents. Titration of dimethylbenzoylsulphanilamide, sulphisoxazole [sulphafurazole] and sulphadimidine in a mixture of methanol and benzene and in pyridine.** Yoshio Tajika and Makoto Aikawa

(Chugai Pharm. Co. Ltd., Takada-minami-cho, Toshima-ku, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (10), 1125–1126.—Titrations of sulphanilamide in glacial acetic acid, pyridine and a mixture of benzene and methanol were investigated. Acidimetric titration with $HClO_4$ (crystal violet as indicator) gives values that are low, presumably owing to the acetylation of the amino group on the benzene ring. N^1-3:4-Dimethylbenzoylsulphanilamide, sulphafurazole and sulphadimidine are quantitatively titrated with Na methoxide, both in pyridine and in a mixture of benzene and methanol (2 + 1), with thymol blue as indicator. The results are statistically analysed; the standard deviation from the mean is $\simeq \pm$ 0·3 per cent. The end-point is clearer in pyridine. K. SAITO

2277. **Syntheses and analyses of isomers of diacetyl derivatives of sulphaguanidine.** Hidehiro Yoshida (Sumitomo Chem. Co. Ltd., Kasugade, Konohana-ku, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (10), 1112–1116.—Two isomers of N^4-acetylsulphanilyl-3-acetylguanidine, the α form (**I**) and the β form (**II**), were synthesised by acetylation of N^4-acetylsulphaguanidine and the guanidine salt of acetylsulphanilic acid, respectively. When **I** is decomposed with an alkaline-earth hydroxide, sulphanilamide and urea are produced, and the urea gives rise to 2 mol. of NH_3. **II**, on the other hand, produces one mol. each of sulphanilic acid, NH_3 and urea, giving 3 mol. of NH_3 altogether. The two isomers are thus determined by the Kjeldahl method in the absence of each other. The sample (30 mg) is treated with $Ba(OH)_2$ (50 to 70 g) and water (300 ml) and the distillate (600 ml) is absorbed in a known amount of 0·1 *N* H_2SO_4 by steam-distillation. K. SAITO

2278. **Chemical assay of diethylstilboestrol [stilboestrol].** R. L. Dryer (Iowa State Univ., Iowa City, U.S.A.). *Clin. Chem.*, 1956, **2** (1), 25–30.—*Prep. of tissue extract*—Samples of cut tissue are homogenised with 15 to 20 vol. of acetone - ether (1:1) and the soln. is filtered through Whatman No. 3 paper previously wetted with solvent. The paper is washed twice with small vol. of solvent and the combined filtrates are adjusted to a convenient vol. Aliquots containing approx. 0·1 mg of stilboestrol (**I**) are evaporated to dryness, the residues are treated with 5 ml of ether, transferred to separating funnels and shaken vigorously with 1 ml of 2·5 *N* NaOH. The separated NaOH soln. is washed twice with 5 ml of ether and the ether is discarded. One ml of 5 *N* H_2SO_4 is added slowly to the alkaline soln. The soln. is cooled under the tap and is then shaken with 5 ml of ether which is separated and evaporated to dryness. *Colorimetric assay*—The residue is dissolved in 1 ml of glacial acetic acid; 1 ml of acetic acid for the blank and 1 ml of standard soln. (0·1 mg of **I** per ml in glacial acetic acid) are put up with each series of tests. Bromine reagent (0·1 ml) (1 per cent. v/v in glacial acetic acid) is added to each tube, the tubes are placed in boiling water for exactly 2 min., removed and cooled under the tap. The contents of the tubes should be pale yellow, indicating free Br; colourless soln. must be discarded as the complex does not form in the absence of free Br. To the cooled soln. add 2 ml of 95 per cent. ethanol and mix; add 3 ml of water, mix well and read the extinction of the rose or violet colour at 500 mμ 1 min. after the water is added. H. F. W. KIRKPATRICK

2279. **The unreliability of the official assay for tablets of glycerol trinitrate.** F. G. Stock and L. W. Hinson (City Analyst's Lab., Birmingham, England). *J. Pharm. Pharmacol.*, 1956, **8** (2), 134–143.—A comparison of the assay procedures of the B.P. and the U.S.P. for tablets of glycerol trinitrate (**I**) has shown that there is a danger of low results with the former owing to failure to extract "bound" **I**. The recovery of **I** by the B.P. method is $\simeq$92 per cent. of the "free" **I**, but is influenced by the tablet size and the percentage of cocoa in the base. The colour of the KNO_3 standard must be developed in the presence of glacial acetic acid, as specified in the B.P. A. R. ROGERS

2280. **A new method for the determination of small quantities of quaternary ammonium compounds.** R. Reiss (Byk-Gulden Lomberg Ges., Konstanz, Germany). *Arzneimittel-Forsch.*, 1956, **6** (2), 77–79.—Quaternary ammonium compounds are quant. converted by KI into iodides; these are extracted with chloroform from acid or alkaline solution and the iodide is oxidised by HNO_2 to iodine, which is estimated colorimetrically. If alkaloids which form chloroform-soluble iodides are present the extraction must be done from alkaline solution. Cetylpyridinium chloride, cetyltriethylammonium bromide and benzyldodecyldimethylammonium bromide can be estimated, whilst tetraethylammonium bromide and similar compounds do not react. As the iodides of dibenzyldi*cyclo*hexylammonium chloride and benzylcetyldi*cyclo*hexylammonium bromide can only be extracted from acid solutions, certain alkaloids interfere in their determination. The method can be used to determine quaternary ammonium compounds in pharmaceutical and cosmetic preparations. To from 0·5 to 2 mg of compound in 10 ml of water add either 1 ml of H_2SO_4 (10 per cent.) or 1 ml of NaOH soln. (10 per cent.) followed by 2 ml of KI soln. (10 per cent.) and extract with 10, 5 and 5 ml of chloroform. To an aliquot of the combined chloroform extracts add water (20 ml), H_2SO_4 (10 per cent.) (1 ml) and $NaNO_2$ (1 per cent.) (5 ml). Shake for 2 min. and measure the extinction of the red chloroform layer. Calibration curves can be prepared from KI. P. S. STROSS

2281. **The determination of formaldehyde in catgut.** D. H. S. Forbes, J. Hunter and P. Lawrie (Ethicon Suture Lab. Ltd., Bankhead Avenue, Edinburgh, Scotland). *Chem. & Ind.*, 1956, (7), 129–131.—Two methods of making routine determinations of formaldehyde in small samples (0·1 to 0·2 g) of surgical catgut are described: (*i*) by microdiffusion—in which the sample and 1 ml of 4 *N* H_2SO_4 are placed in the inner chamber of a Conway micro-diffusion unit, with 2 ml of chromotropic acid soln. in the outer chamber. The unit is sealed and heated in an oven at 110° C for 2·5 hr.; when cool, the chromotropic acid soln. is made up to 25 ml with H_2O, and the colour reading is then made in a Spekker absorptiometer with an Ilford 606 filter; (*ii*) by distillation—in which a modified Highberger - Retzsch apparatus having ground-glass joints is used. The sample plus dil. H_2SO_4 (1 ml) are put in the 10-ml flask and 5 ml of chromotropic acid soln. in the absorption tube. A slow current of formaldehyde-free air is passed through the apparatus and the flask is heated at $\simeq$ 140° C for 45 min. (oil-bath), after which the absorption tube is detached and heated at 110° C (oven) for 100 min. to develop the colour. The soln. is then diluted to

25 ml and the colour reading made in the absorptiometer. The formaldehyde content is calculated (with an error of 2·06 μg) from a standard calibration line. The two methods give concordant results, but (*i*) is more convenient for routine tests. The catgut samples should be initially equilibrated with air at 58 per cent. R.H. W. J. BAKER

See also Abstracts 2143, 2307, 2314, 2318, 2328, 2348.

Food

2282. **Analysis of glucose syrups.** L. Robinson-Görnhardt. *Die Stärke*, 1955, **7**, 305–310.—A comparison was made between three different methods available for the estimation of saccharides contained in glucose syrups, which were produced by acid hydrolysis of starch. (1) Method of Bleyer-Sichert, which determines glucose only, with a modified Fehling solution. Maltose and higher dextrins can be calculated by difference from the total reducing value. (2) Quantitative paper-chromatographic analysis of constituents. (3) Selective fermentation with micro-organisms. Results show that methods (1) and (2) give good agreement for glucose values only. Maltose and dextrin values given by (1) only approximate to those from method (2). Analysis of dextrins after microbiological fermentation of glucose and maltose gives values comparable with method (2) for maltotriose and higher saccharides. The average degree of polymerisation of the dextrin fraction is computed and used to characterise this fraction according to its degree of conversion. Results of paper chromatography show that the difference between various syrups is due not only to a variation of the average degree of polymerisation but also to the actual content of dextrins. E. DUX

2283. **Microscopic examination of modified starches.** T. J. Schoch and E. C. Maywald (Corn Products Refining Co., Argo, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 382–387.—A scheme for the analytical characterisation of modified starches by various microscopic techniques is presented. The examination includes a preliminary inspection, granule counting in a haemocytometer and granule-size distribution. The species of a pregelatinised starch is determined by destroying the material with an enzyme and examining the ungelatinised residue; the gelatinisation temp. is measured by means of the Koffler hot-stage. Ionised starches are identified by dye-adsorption techniques. G. P. COOK

2284. **Determination of the type of meat present in raw-meat products.** O. Bonnand and J.-P. Thiery. *Ann. Falsif.*, 1955, **48**, 163–164.—A technique is described for the detection of different types of meat, in which a standard anti-serum, prepared from known kinds of meat, is used. A standard is obtained by making a maceration of the meat in physiological saline which is then filtered, coagulated by heat and thoroughly mixed. A series of three or four injections at two-day intervals with this coagulum is made beneath the skin of a rabbit. After a further 10 days up to 60 ml of blood are obtained from the animal's heart and centrifuged. The clear serum is preserved in ampoules at between 0° and 4° C. The strength and specificity of the serum should be judged before each test by reaction with macerations of associated and non-associated meats. *Procedure*—Make a maceration of the sample in NaCl soln. (0·5 per cent.) to contain $\geqslant$ 1 g of dissolved protein per litre when the suspension has been pptd. by addition of trichloroacetic acid soln. (30 per cent.). Place 1 ml of the clear liquid in an agglutination tube and add the anti-serum slowly at the bottom of the tube (by means of a capillary tube) to form a second layer with a sharp interface. When a protein antigen and the corresponding anti-serum are present together, a white ppt. forms as a ring at the junction of the liquids after 5 to 10 min. The method can be made roughly quantitative. D. G. FORBES

2285. **Quantitative estimation of carnosine [in meat extracts] by paper chromatography.** P. Tempus and O. Högl (Eidg. Gesundheitsamt, Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (6), 527–536.—Solutions of the extracts and standard amounts of carnosine in 10 per cent. *iso*propyl alcohol are chromatographed with 60 per cent. α-picoline as the solvent. The chromatograms are sprayed with a modified Pauly reagent and evaluated by Sulser's method (*cf. Brit. Abstr. C*, 1953, 365). An average accuracy of $\pm$ 2·8 per cent. is claimed between duplicates, with a 94 per cent. recovery of added carnosine. Results obtained by this method show that carnosine nitrogen forms 10 to 20 per cent. of the total nitrogen in samples of beef, mutton and whale-meat extracts, but values for chicken meat are much lower. W. H. PARR

2286. **Detection of cane sugar in milk and its products.** S. N. Mitra and S. C. Roy (W. Bengal Public Health Lab., Calcutta, India). *J. Indian Chem. Soc., Ind. Ed.*, 1955, **18** (3), 168–173.—A slightly modified Seliwanoff test is described for the detection of added sucrose in milk, milk powder and reconstituted milk. *Procedure*—To 5 ml of modified Seliwanoff reagent [1·0 g of resorcinol in 100 ml of diluted HCl (1:1·5)] is added 1 ml of milk serum (obtained by adding 1 ml of conc. HCl to 25 ml of milk, allowing to stand for 10 min. and filtering) and the mixture is heated in a boiling-water bath for exactly 1 min. An immediate red colour indicates the presence of sucrose or a ketose sugar. The test will detect as little as 0·25 per cent. of added sucrose, whilst avoiding the false positive reactions obtained with boiled or reconstituted milk when acid diluted 1:1 is used. Sensitivity is decreased with acid diluted 1:2. S. C. JOLLY

2287. **The determination of sodium in cheese. II.** F. T. van Voorst (Keuringsdienst voor Waren, Alkmaar, Holland). *Chem. Weekbl.*, 1956, **52** (8), 123.—In this modification of the method previously published (*Brit. Abstr. C*, 1950, 417) the procedure recommended for the determination of Na in "salt-free" cheese involves heating the sample in a platinum basin followed by an elaborate method of extraction. The Na is finally pptd. by Kahane's method (*Rec. Trav. Chim.*, 1940, **59**, 735) as magnesium uranyl acetate. Comparative figures show that the new method gives higher results than the old one. P. HAAS

2288. **Reichert-Meissl numbers of butter fat from commercial products produced in Kansas.** W. D. Rutz, W. H. Martin and C. H. Whitnah (Kansas Agric. Expt. Sta., Manhattan, U.S.A.). *J. Dairy Sci.*, 1955, **38** (4), 387–390.—In a one-year survey of 105 butter-fat samples the mean Reichert-Meissl value was 28·40 (range, 27·05 to 30·10) and

for the butter fat from 169 ice-cream samples taken during one month the mean was 29·19 (range, 27·40 to 31·35). W. H. C. SHAW

2289. **Tocopherol content of Canadian butter fat and its use in detecting adulteration.** C. Anglin, J. H. Mahon and R. A. Chapman (Dept. Health and Welfare, Ottawa, Canada). *J. Dairy Sci.*, 1955, **38** (4), 333–339.—In a one-year survey of the tocopherol contents of 329 samples of Canadian commercial butter fats by the method described previously (*Anal. Abstr.*, 1954, **1**, 2822), the average monthly tocopherol contents from June to May were 34, 40, 42, 42, 42, 31, 27, 21, 19, 19, 21 and 26 p.p.m. (mean 31; overall range 10 to 50 p.p.m.). Confidence limits for the max. content of summer (July to Oct.) butter-fat were 95 per cent. below 49, 99 per cent. below 52, and 99·95 per cent. below 57 p.p.m., and for winter (Jan. to Apr.) butter-fat below 27, 30 and 35 p.p.m., respectively. In an example given, the tocopherol content clearly indicated adulteration when it could not be detected by the Reichert - Meissl and Polenske procedures. W. H. C. SHAW

2290. **Tocopherol content of the fat of dairy products as an index of adulteration.** J. H. Mahon, C. Anglin and R. A. Chapman (Dept. Health and Welfare, Ottawa, Canada). *J. Dairy Sci.*, 1955, **38** (10), 1089–1095.—The tocopherol method described previously for butter fat (*Anal. Abstr.*, 1954, **1**, 2822) is extended to the examination of fat from evaporated and condensed milk, whole-milk powder, ice-cream and cheese; modified extraction procedures are described for each. The method will not detect the presence of lard, tallow or coconut oil, is not applicable to chocolate ice-cream and may give high results if dyes, other than those detailed, are present. An examination of 6270 butter-fat samples gave a mean tocopherol content of 31 p.p.m., all except one being between 2 p.p.m. and 50 p.p.m., the Canadian permitted limit. Examples are given of the effectiveness of the method in detecting adulteration in dairy products. W. H. C. SHAW

2291. **A tentative method for the detection of hydrogenated oils in ghee by the estimation of *iso*-oleic acid content.** R. Narayanan and A. R. S. Kartha (Agric. Res. Inst., New Delhi). *J. Sci. Ind. Res., B, India*, 1955, **14** (10), 544–546.—The method suggested is a modification of the Twitchell separation (*Ind. Eng. Chem.*, 1921, **13**, 806; *cf.* Williams and Bolton, *Analyst*, 1924, **49**, 460). Several samples of ghee and vanaspati have been analysed. The ghee contains 3 to 5 per cent. of *iso*oleic acid and the vanaspati has much higher amounts. It is shown that individual *iso*oleic acids can be estimated accurately, but if the ghee acids are mixed with those from other oils the results are variable. With mixtures of ghee and vanaspati there is a progressive increase in *iso*oleic acid content and iodine value as the proportion of vanaspati is increased; agreement is poorer as the amount of *iso*oleic acids from vanaspati increases. The iodine values of solid acids from mixtures of ghee and vanaspati show a progressive increase as the proportion of vanaspati in the mixture increases, but the increase in iodine value is not proportional to the amount of vanaspati. The conclusions drawn are that when ghee contains 5 per cent. or more of *iso*oleic acids or gives an iodine value of 12 or more for solid acids, it is likely to be adulterated with hydrogenated oils. C. A. SLATER

2292. **Quick field method for the estimation of starch in banana pseudostem.** N. L. Jain, Girdhari Lal and V. Subrahmanyan (Central Food Tech. Res. Inst., Mysore, India). *J. Sci. Food Agric.*, 1956, **7** (1), 61–65.—A representative sample (10 g), taken from the middle portion of the plant, is crushed in a mortar; 10 ml of 3 *N* NaOH are added gradually and the crushing is continued. After a thorough mixing, 30 ml of water are added to make the total vol. $\simeq$50 ml. The extract is filtered through a piece of silk cloth and the temp. of the filtrate is adjusted to $\simeq$26° C. A simplified form of Ostwald's viscometer was used for determining the rate of flow of soln. of starch in aq. NaOH. The time required for the flow of a specific vol. of the filtrate between two marks is determined. From a graph indicating the relationship between percentage concn. and time of flow of starch soln. through the viscosity pipette, the percentage concn. of the starch in the filtrate is directly read. S.C.I. ABSTR.

2293. **Potentiometric estimation of formol numbers [of fruit juices].** O. Wyler (Eidg. Gesundheitsamt, Bern). *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (6), 515–524.—The determination of amino acids in fruit juices by the formol titration method has been observed potentiometrically, and the results compared with those obtained with indicators. The following procedure has been found to give satisfactory results. Mix the juice (20 ml) with H_2O (50 ml) in a 100-ml flask. Add 25 per cent. $CuSO_4.5H_2O$ (5 ml) and 25 per cent. $K_4Fe(CN)_6.3H_2O$ (5 ml), shake, make up to the mark and filter. Titrate 25 ml of the filtrate to a pH of 8·5 with 0·1 *N* NaOH, add 40 per cent. formaldehyde soln. (10 ml) (previously adjusted to pH 8·5) and then titrate to pH 9·0. Possible sources of error are discussed. W. H. PARR

2294. **The study and estimation of dehydracetic acid in beverages.** J. A. Gautier, J. Renault and H. Ghadichah. *Ann. Falsif.*, 1956, **49**, 7–21.—Details of a general method for the estimation of dehydracetic acid (3-acetyl-6-methylpyran-2:4-dione) (**I**), based on the colour produced with salicylaldehyde, are standardised. *Procedure*—(*a*) *Preliminary extraction*—Mix the sample (20 ml, or 50 ml for a qual. examination) with *N* NaOH (2 ml or 5 ml, respectively) and evaporate to dryness in a vacuum-desiccator containing conc. H_2SO_4. Take up the residue with three portions of water (3 ml) and transfer to a mortar. Add conc. HCl (1 ml) and silica gel (7·5 g) and mix carefully. Suspend the resulting powder in chloroform (40 ml) (freshly washed five times with water and dried over anhydrous Na_2SO_4) and transfer to a 20-cm chromatographic column of silica gel. Rinse the mortar with chloroform (3 × 10 ml) and pour the washings through the column. Draw the whole of the solvent through with final gentle suction. Extract the chloroform with 0·1 *N* NaOH (5 × 4 ml) and make up the combined extracts to 20 ml. Remove traces of chloroform with a gentle stream of air. (*b*) *Estimation*—To the prepared sample soln. (5 ml) in a flask, add NaOH soln. [40 per cent. NaOH soln. (1 vol.), water (1 vol.)] (5 ml) and salicylaldehyde soln. (20 per cent. in purified ethanol) (2 ml). Affix an air condenser and immerse the flask immediately in a water bath at 75° $\pm$ 0·2° C for exactly 1 hr. Wash the cooled contents with ethanol (70 per cent.) and dilute to 25 ml. Estimate **I** by comparing the extinction

at 540 mμ in a 1-cm cell with that of a blank preparation and standard soln. with the pure compound. The temperature and time of reaction, concn. of reagents, the solvents and wavelength are critical, but the colour produced is stable for 2 hr. Errors due to the colour of the extract and to normal interfering substances are negligible. (*c*) *Characterisation*—Of the available methods (preparation of the copper salt, of the 2:4-dinitrophenylhydrazone, melting point or microscopic examination of the sublimed crystals) the last is considered most dependable, and will detect 100 μg of **I**.

D. G. FORBES

2295. **Measurement of the surface tension of beer by the drop-weight method.** A. D. Rudin (Brewing Ind. Res. Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 1956, **62** (1), 27–30.—A modification of the drop-weight method for the determination of surface tension of beer is described. An Agla micrometer syringe unit with a Monel-metal drop-tube attached was used. The drops were allowed to form at 20° C in an atmosphere in equilibrium with the liquid under test, by enclosing the dropping tube in a 100-ml flask containing some of this liquid; pressure equilibration was maintained by a small longitudinal groove in the rubber bung. The volume (ml) of the drops was calculated from the difference of micrometer readings between subsequent drops. The surface tension was calculated from the classical formula. An apparent reduction in the surface tension with increase in the time taken for the determination is reported.

G. H. BAKER

2296. **Evaluation of hops. III. Convenient method for polarimetric determination of the α-soft resin of hops.** R. D. Hall (Brewing Ind. Res. Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 1956, **62** (1), 16–19.—The Ford and Tait classical method of hop analysis is modified by treatment of the methanolic solution of the hop with a selected activated carbon. This removes the interfering substances and renders the polarimetric determination of the total "humulones" more accurate. The removal of the interfering substances by the activated carbon improves the stability of the methanolic hop extract. *Procedure*—The standard Ford and Tait unfiltered methanolic solution (100 ml) is mixed with the selected activated carbon (1 g) and allowed to stand, with occasional shaking, for approx. 15 min. The adsorbent is removed by filtration, and the rotation is measured in a 1-dm tube. The value of − 206·24° as the $[\alpha]_D^{20}$ of humulone in methanol was used in the calculation of the α-resin contents.

G. H. BAKER

2297. **Charcoal method for estimation of the content of humulones in hops.** W. H. Gough (Stag Brewery, Pimlico, London). *J. Inst. Brewing*, 1956, **62** (1), 9–15.—Good agreement is reported between this method, in which a charcoal column is used, and established methods. The procedure does not appear to be affected by the type of charcoal used, and can be applied to both old and new hops. A 100-ml Soxhlet extractor is packed to a depth of ≃ 7 cm with a mixture of charcoal (1 g) and kieselguhr (6 g). The prepared Soxhlet extractor is washed with ether containing SO_2 (to eliminate oxygen adsorbed on the charcoal), then the ground hops (10 g) are introduced, and the whole is extracted with ether for 1·5 to 2 hr. The ether is distilled off, and the residue is dissolved in *n*-pentane. An aliquot is centrifuged at 2500 r.p.m. and the optical rotation of the clear liquid is measured in a 4-dm tube. The humulone content is calculated by using $[\alpha]_D$ for humulones in *n*-pentane of − 231°.

G. H. BAKER

2298. **Evaluation of hops: new approach to the detailed analysis of hop resins.** G. A. Howard and A. R. Tatchell (Brewing Ind. Res. Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 1956, **62** (1), 20–27.—A rapid and accurate method for the determination of cohumulone, humulone and adhumulone in hop resins is given. The fatty acids obtained by oxidising the α-soft resin of hops are determined by gas - liquid partition chromatography. The amount of the corresponding colupulone, lupulone and adlupulone in the "β-acids" may be determined either in the same manner or by using liquid - liquid partition chromatography. Satisfactory agreement is reported between this method and the more time-consuming counter-current distribution method.

G. H. BAKER

2299. **Determination of volatile sulphur compounds. IV. Further notes on mercaptans [in brewing materials].** M. W. Brenner, J. L. Owades and T. Fazio (Schwarz Lab. Inc., Mount Vernon, New York, U.S.A.). *Proc. Amer. Soc. Brew. Chem.*, 1955, 125–132.—An olfactory test, based on the screening of the odour of both H_2S and mercaptans by $CuSO_4$ soln., and of H_2S, but not mercaptans, by $CdSO_4$ soln., is described; the test enables the influence of mercaptans and H_2S in the odour of beers to be assessed. A simplified method for the quant. determination of mercaptans is described. *Procedure*—The sample is distilled after the addition of a small amount of Cd acetate, the distillate is buffered with phosphate buffer soln. (pH 7) (2 ml per 100 ml) and a soln. of colloidal S is added. The soln. is then heated to 30° C and N is swept through for 1 hr., bubbling the gases through 2 per cent. aq. Zn acetate (20 ml) in a graduated cylinder, after which 2·5 ml of a 50 per cent. soln. of *p*-aminodimethylaniline sulphate in dil. H_2SO_4 and 0·5 ml of aq. $FeCl_3$ (2·7 per cent.) are added and the contents of the cylinder made up to 25 ml with Zn acetate soln. The colour is read in a spectrophotometer or colorimeter. The mercaptan contents of various brewing materials and beers are reported and the related reactions are discussed.

V. Sulphur dioxide. M. W. Brenner, J. L. Owades and T. Fazio. *Ibid.*, 1955, 133–144.—Sulphur dioxide is determined in beer by reduction with $SnCl_2$ to H_2S, which is then determined colorimetrically after conversion into methylene blue by absorption in Zn acetate soln. and reaction with *p*-aminodimethylaniline and $FeCl_3$ (*cf.* Part IV). The procedure is effected by passing a stream of N through a series of wash-bottles containing, first, the sample and $SnCl_2$, then phosphate buffer (pH 7) and, finally, 2 per cent. aq. Zn acetate. The SO_2 contents of various brewing materials and beers are reported and it is shown that SO_2 is formed during fermentation. The relationship between SO_2 content and various sulphur compounds in beer and the concept of "free" and "bound" SO_2 are discussed. Results obtained by the procedure described are generally lower than those obtained by the Monier - Williams method, which is considered to be subject to appreciable positive errors. At < 20 p.p.m. of SO_2, the effect on the odour of beer is undetectable.

S.C.I. ABSTR.

2300. **Determination of the sulphur content of yeast.** H. Suomalainen and A. J. A. Keränen (ALKO, Itämerenkatu 51, Helsinki, Finland). *Z. anal. Chem.*, 1955, **148** (2), 81–91.—Sulphur in yeast is determined by the Klingstedt procedure recommended for estimating S in cellulose, whereby the sample is dissolved in fuming HNO_3 with MgO as catalyst, and the sulphate is determined as $BaSO_4$. J. H. WATON

2301. **Standard for the total acidity of wines.** P. Jaulmes. *Ann. Falsif.*, 1955, **48**, 157–163.—A procedure is described for the measurement of the total acidity of wines as defined by the sub-committee of the International Wine Office (*i.e.*, the acidity measured during neutralisation of the wine with alkali to pH 7·0). A standard end-point colour is prepared in a 12-cm crystallising dish containing boiled distilled water (25 ml), bromothymol blue indicator (4 g per litre in 20 per cent. neutral ethanol) (1 ml) and the de-gassed sample (5 ml). To the mixture is added enough 0·05 *N* NaOH to produce a colour change to greenish blue, followed by 5 ml of a buffer soln. of pH 7·0 [KH_2PO_4 (107·3 g) in *N* NaOH soln. (500 ml) diluted to 1 litre with water]. The determination is carried out by titrating a mixture of boiled water (30 ml), bromothymol blue indicator (1 ml) and the sample (degassed) (5 ml) with 0·05 *N* NaOH soln. to produce an identical colour. Acidity due to CO_2 and SO_2 is not to be included. The CO_2 is eliminated by agitation of the cold sample under reduced pressure. Correction is made for free SO_2 and that combined with sugars and with acetaldehyde by estimating the free SO_2 and combined SO_2 in the distillate from the determination of the volatile acidity, and deducting the appropriate equivalent from the original alkali titration. D. G. FORBES

2302. **Polarimetric estimation of malic acid in musts and wines.** E. Matthey and A. Ramuz (Lab. Cantonal, Lausanne, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (6), 503–508.—A method for the polarimetric estimation of malic acid by the very active compound which it forms with ammonium molybdate has been adapted for use with must and wine. Tannins, pectin, etc., are pptd. with $ZnSO_4$ after the removal of tartrates, and the malic acid is pptd. as the barium salt. This is decomposed with H_2SO_4 and the supernatant liquid, after being centrifuged, is treated with ammonium molybdate soln. The method is suitable for routine work and it is accurate to approx. 0·1 g per litre. W. H. PARR

2303. **A new technique for the estimation of potassium in wines by precipitation as acid tartrate.** L. Deibner and P. Benard. *Ann. Falsif.*, 1955, **48**, 165–180; 217–222.—A study is made of conditions influencing the pptn. of K as bitartrate by the method of Iévinsch and Ozol (*Brit. Abstr. C*, 1953, 377). The influence of $Ca^{\cdot\cdot}$, $Na^{\cdot}$, $Mg^{\cdot}$, NO_3', SO_4'', Cl' and PO_4''' present in the quantities found in wines is negligible; PO_4''' may be present in large amount. *Procedure*—Destroy the organic matter in 25 to 50 ml of the sample of wine (containing $\leqslant$ 12·5 mg of K) by evaporation to dryness on a sand bath with H_2O_2 (110 vol.) (10 ml) and conc. HNO_3 (5 ml). Repeat the process with H_2O_2 (5 ml) and HNO_3 (2 ml). Extract the residue with water (5 × 15 ml) and evaporate the filtered extract to 5 ml on a sand bath and finally on a water bath. Add methanol (5 ml), methyl orange indicator (0·2 per cent.) (1 drop) and just acidify with HCl. Add, dropwise, a soln. of aniline tartrate reagent [tartaric acid (20 g) in water (500 ml) and freshly distilled aniline (8 g), made up to 1 litre with methanol] until the colour changes to yellow. After a short time add a further 2 ml of reagent. Stand the beaker in ice for $\leqslant$ 2 hr. Filter and wash the ppt. with methanol (5 × 10 ml). The tartrate ppt. is evaluated by dissolution in hot water (recently boiled), and titration with 0·05 *N* NaOH (CO_2-free), with phenolphthalein as indicator. The procedure is standardised by similarly treating a soln. of a pure potassium salt. D. G. FORBES

2304. **Comparative study of some methods for the estimation of potassium in wines.** J. Bonastre (Station Agronomique et Oenologique de Bordeaux, France). *Ann. Falsif.*, 1955, **48**, 347–351.—A comparison, with the experimental results, is given of the following methods for the determination of K in wines. (*a*) The method of Pasteur and Raboul, (*b*) sodium cobaltinitrite, (*c*) sodium tetraphenylboron, and (*d*) flame photometer. Conditions for (*b*), (*c*) and (*d*) are detailed. Methods (*c*) and (*d*) proved most accurate and consistent; (*a*) and (*b*) gave slightly high results. In the absence of a flame photometer, which gives very quick results, method (*c*) is the most economical in time and labour. D. G. FORBES

2305. **The estimation of acetaldehyde in wines and similar beverages.** I. Mareca Cortes and M. de Campos Salcedo. *Ann. Falsif.*, 1955, **48**, 479–483.—Experiments with wines containing $\geqslant$ 98 g of reducing sugars per litre showed that borate is ineffective as a buffer during distillation. There is a lowering of the pH, marked caramelisation and a positive error when acetaldehyde is estimated in the distillate iodimetrically. The following method was evolved and proved the most satisfactory. Neutralise the sample (25 ml) with *N* NaOH soln., with phenolphthalein as indicator. Add a phosphate buffer [$Na_2HPO_4.2H_2O$ soln. (1·1876 per cent. w/v) (96·9 ml) plus KH_2PO_4 soln. (0·9078 per cent. w/v) (3·1 ml)] (25 ml). Distil under a reduced pressure of 45 cm (Hg). Express the content of acetaldehyde in the distillate as ml of 0·02 *N* I soln. absorbed. D. G. FORBES

2306. **Investigation of the extraction of salicylic acid and benzoic acid from wine by steam-distillation.** M. P. Archinard (Station Oenologique de Beaune, France). *Ann. Falsif.*, 1955, **48**, 213–217.—Experiments with dilute soln. show that with steam-distillation at 100° C, 65 per cent. of salicylic acid (**I**) and 94 per cent. of benzoic acid are removed with the first 150 ml of the distillate. With a temperature of 110° to 120° C, $>$ 96 per cent. is recovered in both cases. The liquid in the flask must be first acidified with tartaric acid. The collection of **I** is best made by incorporating a 'scrubbing' device containing water (2 ml). In the absence of **I**, benzoic acid is collected in the scrubber, which should contain some *N* NaOH (0·5 ml), and is converted into **I** and tested as follows (Dubaquie). The scrubbings (5 ml) are neutralised in a test-tube with *N* H_2SO_4, and glacial acetic acid (0·5 ml), H_2O_2 (10 vol.) (0·5 ml), invert-sugar soln. (5 per cent.) (6 ml) and $CuSO_4$ soln. (20 per cent.) (0·5 ml) are added. The tube is immersed for 15 min. in a boiling-water bath, then cooled, and the dissolved **I** is extracted with benzene. The extract,

after being washed with water (2 ml), is shaken with water (1 ml) and ferric alum soln. (1 per cent.) (1 drop). A violet or rose colour in the aq. phase indicates **I**. D. G. FORBES

2307. **Paper electrophoresis of mixtures of saccharin and dulcin.** A. Castiglioni (Univ. Turin, Italy). *Z. anal. Chem.*, 1955, **148** (2), 98–99.—Excellent results are achieved in the separation of saccharin and dulcin by paper electrophoresis, by employing a 10 per cent. v/v soln. of acetic acid as solvent. A strip of Whatman No. 1 paper (34 cm × 5 cm) is used, to which the material is applied ≃ 13 cm from one end. A current of 0·4 mA per cm is passed for 2 hr. After drying, the strip is sprayed with HNO_3 - acetone (1:4, v/v), when dulcin, which remains at the point of application, shows up as a yellow spot that turns brown when neutralised with aq. NH_3. Saccharin is revealed with a 0·1 per cent. soln. of 1-naphthylamine in 95 per cent. ethanol to which 4 to 5 drops of saturated aq. copper acetate soln. and 2 to 3 drops of glacial acetic acid are added. The violet - blue saccharin spot is located by drying the paper ≃ 10 cm from the point of application. J. H. WATON

2308. **Analysis of technical monoglycerides with potassium periodate.** L. Hartman (Fats Res. Lab., D.S.I.R., Wellington, New Zealand). *Analyst*, 1956, **81**, 67–68.—The reagent commonly used in the analysis of technical monoglycerides is a soln. of HIO_4 or $NaIO_4$ in acetic acid. A modification of the method is now described in which the HIO_4 is replaced by KIO_4 dissolved in a little 10 *N* H_2SO_4 and diluted with acetic acid. A mixture of pyridine and acetic acid is added to the chloroform used for dissolving the monoglycerides, thereby preventing their decomposition by the H_2SO_4. After reaction with the oxidising mixture in the dark for 30 min. the residual IO_4' is determined by the addition of KI and titration of the liberated I with standard $Na_2S_2O_3$. In the determination of uncombined glycerol the sample soln. in the chloroform - pyridine - acetic acid solvent is shaken with water, aq. KIO_4 soln. is added and after reaction the residual IO_4' is determined as before. In both analyses blank determinations are made concurrently with the solvent mixture only, calculations being dependent on the difference in the titres of blank and sample. The reproducibility is within ≃ ± 0·5 per cent. for monoglycerides and ≃ 0·2 per cent. for glycerol. A. O. JONES

2309. **The estimation of 1-monoglyceride [in fats].** C. M. Dowse and J. A. Saunders (Med. Sch., King's Coll., Newcastle upon Tyne, England). *Biochem. J.*, 1956, **62** (3), 455–458.—The method described is based on the determination of the formaldehyde produced by oxidation with HIO_4, and eliminates uncertainties that occur in the titration method of Pohle *et al.* (*Brit. Abstr. BII*, 1950, 813). The procedure is similar to that of Corcoran and Page (*J. Lab. Clin. Med.*, 1948, **33**, 1326), but the acetic acid in the oxidation mixture is replaced by propionic acid, the chloroform is removed by aeration under reduced pressure, and steam is used together with distillation to remove the formaldehyde, which is determined colorimetrically by the chromotropic acid method. J. N. ASHLEY

2310. **Determination of the iodine value of vegetable oils.** I. Ubaldini and F. Capizza Maitan (Ist. Chim. Ind. Politecnico, Società Montecatini, Milan, Italy). *Chim. e Ind.*, 1955, **37** (12), 943–945.—Results of the determination of iodine value of vegetable oils with I in CCl_4 in the presence of mercuric acetate agree well with those from the method of Wijs and the method of Gallo, Weise and Nelson (*Ind. Eng. Chem.*, 1948, **40**, 1277) for the determination of isoprene - *iso*butylene polymers. In most instances, with 0·15 to 0·25 g of oil and 0·1 *N* I in CCl_4 the reaction is complete in 10 min., and back-titration can then be performed. With linseed oil and castor oil, the reaction takes about 1 hr. C. A. FINCH

2311. **The quantitative determination of vitamin D.** F. Holtz, G. Pfenningsdorf and W. Ponsold (Pharmakol. Inst. Univ. Halle, Germany). *Arzneimittel-Forsch.*, 1955, **5** (10), 557–559.—A rat bio-assay of vitamin D is described. Prophylactic doses of vitamin D are fed to groups of 11 rats (21 to 24 days old and weighing 35 to 45 g) fed on McCollum's diet No. 3143, and the degree of rickets is assessed by X-ray photographs of the epiphyseal line of the tibia. After 14 days the dose conferring protection to 50 per cent. of the animals (SD50) is determined for standard and sample and the vitamin-D potency is calculated. The method is illustrated by an example and is claimed to be more reliable, more rapid, and less costly than the therapeutic test. P. S. STROSS

2312. **Separation of riboflavine and its phosphoric esters by cellulose-column chromatography.** P. Cerletti and N. Siliprandi (Biochem. Dept., Univ. Rome). *Acta Vitaminol.*, 1955, **9**, 145–148.—The use of powdered cellulose as adsorbent permits the clear separation of riboflavine (**I**), riboflavine phosphate (**II**) and riboflavine pyrophosphate (**III**) by column chromatography. *Procedure*—Subject cellulose powder to vacuum to remove gases and suspend in phosphate buffer (pH 7·0); run into glass column (3·5 cm in diam. × 45 cm long), remove buffer, and form the chromatogram by adsorption from aq. soln. containing >1 mg of **I**, **II** and **III** per 4 ml of H_2O. Elute with Na acetate buffer (pH 5·1) or trimethylammonium formate buffer (pH 4·8) at a speed of 30 ml per hr. The original yellow band is split into zones, and the eluate contains **III**, **II** and **I** in this order. Advantages claimed are—definite separation of **I**, **II** and **III** from each other and related compounds; **I**, **II** and **III** are obtained in aq. soln., which may be used for direct spectrophotometric or fluorimetric estimation; if volatile buffer is used, the pure substances may be obtained in the dry state by simple vacuum evaporation. H. A. FISHER

2313. **Studies on the ninhydrin reaction. IV. Determination of pantothenic acid.** Masaharu Yamagishi and Toshiko Yoshida (Takeda Pharm. Ind. Ltd., Juso-Nishino-cho, Higashiyodogawa, Osaka). *J. Pharm. Soc. Japan*, 1954, **74** (10), 1001–1004.—β-Alanine (**I**), resulting from the hydrolysis of pantothenic acid (**II**) in 0·25 *N* HCl, interacts with ninhydrin in the presence of pyridine and ascorbic acid to give a purple colour. The extinction at 570 mμ obeys Beer's law for < 50 μg of **I** in 10 ml. Samples of **II** usually contain a small amount of **I** and separation can be effected by paper chromatography, with water - butanol - acetic acid (5 + 4 + 1). Two portions of the sample soln. (≃ 250 mg of **II**) are submitted to paper chromatography and one is revealed with ninhydrin. The corresponding part of the other chromatogram

is cut out and extracted with 0·25 *N* HCl (5 ml). A 2-ml portion in a stoppered tube is heated on a boiling-water bath for 30 min., then treated with ninhydrin (1 per cent., 1 ml), ascorbic acid (0·5 per cent., 1 ml) and pyridine (1 ml), and the extinction is measured. K. SAITO

2314. **The use of *p*-chloromercuribenzoic acid in the determination of ascorbic acid with 2:6-dichlorophenolindophenol.** J. A. Owen and B. Iggo (Dept. of Clin. Chem., Univ. of Edinburgh). *Biochem. J.*, 1956, **62** (4), 675–680.—The colorimetric determination of indophenol-reducing activity is impracticable below pH 3·5 because of the extent of spontaneous fading of indophenol that occurs. *p*-Chloromercuribenzoic acid does not affect the reaction between indophenol and ascorbic acid, but it inhibits almost entirely the decolorisation of indophenol by various interfering substances. J. N. ASHLEY

2315. **Chemical estimation of vitamin-E activity in cereal products. III. Application of partition chromatography to the isolation of ε-tocopherol from bran and to the determination of the individual tocopherols of cereals.** P. W. R. Eggitt and F. W. Norris (Birmingham Univ., England). *J. Sci. Food Agric.*, 1955, **6** (11), 689–696.—A reversed-phase technique, with a liquid paraffin - aq. ethanol system supported on kieselguhr made unwettable by exposure to dimethyldichlorosilane vapour, was applied to the isolation of ε-tocopherol (5-methyltocol) from bran. The separation of the mixed tocopherols is discussed. For a purely analytical chromatogram, the column is loaded with not more than 0·5 mg of each individual tocopherol, so that Emmerie - Engel determinations may be made directly on the 3-ml fractions in the tubes in which they are collected. In dim artificial light, 0·5 ml of 2:2′-dipyridyl soln. and then 0·5 ml of $FeCl_3$ soln. are added to each fraction; the density of the mixed soln. is measured at 520 mμ exactly 2 min. after the addition of the $FeCl_3$. ε-Tocopherol was isolated in sufficient quantity to study properties and reactions. A comparison of the u.v. absorption spectra of the tocopherols is given. The formation of a yellow nitroso compound by ε-tocopherol with HNO_2, and its absorption spectrum, are discussed. S.C.I. ABSTR.

2316. **Spectrophotometric method for the estimation of vitamin K_3 [menaphthone].** V. Sathe, J. B. Dave and C. V. Ramakrishnan (M.S. Univ. of Baroda, Baroda, India). *Nature*, 1956, **177**, 276.—From 2 to 30 μg of vitamin K_3 in soln. can be determined by a modification of the Reddy - Srinivasan method (*cf. Brit. Abstr. C*, 1948, 154). *Procedure*—Shake the soln. with ethanol (0·5 ml), add 0·1 ml of a saturated soln. of 2:4-dinitrophenylhydrazine in 2 *N* HCl and, after 10 min., 0·25 ml of 20 per cent. aq. Na_2CO_3. Shake the mixture well until the green colour appears, then add *n*-pentanol (3 ml), ethanol (1 ml) and H_2O (1 ml), and shake again. After 5 min. remove the *n*-pentanol layer and measure its extinction at 635 mμ in a 1-cm cell. The colour is stable for 10 hr.; the curve of extinction *vs.* vitamin-K_3 concn. is linear. The method can be applied to the micro-determination of vitamin K in moulds. W. J. BAKER

2317. **Identification of insect fragments: relationship to the aetiology of the contamination.** O. L. Kurtz and K. L. Harris (Div. Microbiol., F. and D.A., Dept. Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1955, **38** (4), 1010–1015.—Photographs of diagnostic fragments of beetles and moths are reproduced. Fragments originating in wheat are usually from the rice or granary weevil, lesser grain borer, flat grain beetle, Angoumois grain moth and saw-toothed grain beetle. In the mill the main sources of contamination are the confused and rust-red flour beetles, and the Mediterranean and Indian meal moths. Stored flour may be contaminated with bran bugs and moths. A. A. ELDRIDGE

See also Abstracts 1974, 2217, 2314, 2347, 2348.

Sanitation

2318. **Monitoring for toxic dusts and fumes.** A.H.C.P. Gillieson (Atomic Energy Res. Estab., Harwell, England). *Atomics*, 1955, **6** (1), 15–18.—Air suspected to contain particles of beryllium oxide or fluoride, or beryl ore, is passed through a copper arc and the Be line at 3130·1 A is isolated by a grating monochromator and measured on an RCA IP28 photomultiplier coupled to a Honeywell - Brown circular chart recorder. This continuously recording instrument detects < 2 μg of Be per cu. metre. E. N. JENKINS

2319. **Recommended methods for the analysis of trade effluents. [Determination of copper and arsenic.]** Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents. *Analyst*, 1956, **81**, 59–63.—Details are given of recommended methods for preparation of the sample of effluent for the determination of metallic constituents by wet oxidation, the determination of As by the Gutzeit method and (for amounts of As from 0·4 to 100 mg) by the hypophosphite method (Haslam *et al.*, *Brit. Abstr. C*, 1953, 422), and Cu by extraction from alkaline citrate soln. as its diethyldithiocarbamate with subsequent spectrophotometric determination. When Bi occurs with Cu the method as described for Cu is repeated but with the addition of KCN soln. before extraction with the carbamate reagent. The extinction of this extract is deducted from that of the first to give the extinction due to Cu. A. O. JONES

2320. **Determination of oxygen dissolved in water.** R. Freier and G. Resch (Inst. anorg. Chem., Tech. Hochsch., Brunswick, Germany). *Z. anal. Chem.*, 1956, **148** (6), 427–434.—A differential iodimetric method is described for the estimation of O present in water up to 500 μg per litre. In the pH range 2·3 to 2·5 there is no interference from atmospheric O, whilst the effect of reducing agents is overcome by employing a blank estimation. *Procedure*—Into one of two samples (500 ml) of the water, 1·5 ml of $MnCl_2$ soln. (800 g of $MnCl_2.4H_2O$ per litre) and 1·5 ml of alkaline KI soln. (prepared by mixing a soln. of 700 g of KOH in 550 ml with a soln. of 150 g of KI in 150 ml) are injected below the level of the neck of the flask by means of a pipette or a micro-burette. After being shaken, the flask is allowed to stand for 5 to 10 min., when a ppt. of a Mn^{IV} compd. appears. The stopper is carefully removed, 5·5 ml of H_2SO_4 (1:1) are added below water level and the flask is well shaken. The Mn^{IV} ppt. dissolves to form $Mn^{\cdots}$. The mixture (500 ml) is poured into a flask which contains 20 ml of Na acetate soln. (450 g per litre), and then ≃1 g of KI, 10 ml of 0·001 *N* I soln. (more for water with a high content of reducing material) and 2 ml of starch soln. are

added. The I is titrated with 0·00625 *N* $Na_2S_2O_3$ soln. by means of a micro-burette. The other sample of water (500 ml) is poured into a flask which contains 20 ml of Na acetate soln. (450 g per litre), and 3·5 ml of H_2SO_4 soln. (1:1), ≃1 g of KI, 10 ml of 0·001 *N* I soln. (more for water with a high content of reducing material) and 2 ml of starch soln. are added. The unchanged I is titrated with 0·00625 *N* $Na_2S_2O_3$. The O is equivalent to the difference between the two vol. of the 0·00625 *N* $Na_2S_2O_3$, 1 ml of which corresponds to 100 μg of O per litre on a sample of 500 ml. J. H. WATON

2321. **Determination of low chemical oxygen demands of surface waters by dichromate oxidation.** W. A. Moore and W. W. Walker (Dept. Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 164–167.—The use of 0·025 and 0·05 *N* $K_2Cr_2O_7$ as oxidant in the estimation of the organic content (chemical oxygen demand) of surface waters by the wet combustion method was studied. Chlorides, some representative organic compounds and organic material found in river waters were oxidised and the results compared favourably with those obtained by the method in which 0·25 *N* $K_2Cr_2O_7$ was used as the oxidant (Moore *et al.*, *Brit. Abstr. C*, 1949, 415). G. P. COOK

2322. **Determination of high-boiling paraffin hydrocarbons in polluted water.** F. J. Ludzack and C. E. Whitfield (Dept. Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 157–160.—The oil is extracted from the water into CCl_4 and is determined by i.r. measurement in the same solvent. Interferences, revealed by the i.r. spectra, are removed by chromatographic separation and a corrected calibration curve is obtained for the specific class of hydrocarbon. Recoveries of added motor oil or octadecane varied between 89·5 and 99·0 per cent., and the coefficient of variation was generally < 21 per cent. G. P. COOK

2323. **Flame-photometric determination of dissolved solids in water.** G. E. Marsh (Standard Oil Co., Whiting, Ind., U.S.A.). *Applied Spectroscopy*, 1956, **10** (1), 8–10.—A flame-photometric method, in which a Beckman DU spectrophotometer with flame attachment and a Model 4300 photomultiplier tube as detector are used, is described for the determination of 30 to 45 p.p.m. of Ca, 5 to 15 p.p.m. of Mg, 5 to 20 p.p.m. of Na and 1 to 2 p.p.m. of Fe in water. An oxy-acetylene flame is used. As Ca and Na affect the determination of Fe and Mg, standards are prepared containing different amounts of each ion in the presence of fixed amounts of the other three. The reproducibility is about 0·1 p.p.m. based on repetitive analyses of three synthetic and three natural samples. No sample preparation is needed and a complete analysis takes about 30 min. No interference is found from HCO_3', SO_4'', NO_3', F′ or Cl′. K. A. PROCTOR

2324. **Determination of anionic detergents in surface waters and sewage with methyl green.** W. A. Moore and R. A. Kolbeson (Dept. Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 161–164.—The anionic detergent is complexed with methyl green dye, the complex is extracted into benzene and the extinction of this soln. is measured. The recovery of added detergent was > 90 per cent. for sewage and > 97 per cent. for surface-water samples, and the standard deviation was ± 0·31 at the 10-μg and ± 0·84 at the 50-μg levels. The method is less subject to interference than that with methylene blue as the complexing agent and is also more accurate and precise. G. P. COOK

2325. **Determination of low concentrations of xanthates in industrial sewage waters.** Yu. Yu. Lur'e and Z. V. Nikolaeva ("Vodgeo" Inst.). *Zavod. Lab.*, 1956, **22** (1), 30–35.—The sample of water (200 ml with xanthate concn. of 0·025 to 1 mg per litre, 100 ml with 1 to 10 mg per litre, and 25 ml with 10 to 90 mg per litre) is carefully neutralised in a separating funnel with 0·1 *N* acid or alkali, the amount necessary being determined by titration of a similar solution, with methyl orange as indicator. Buffer solution (5 to 10 ml), prepared by diluting 42 ml of *M* acetic acid and 158 ml of *M* Na acetate to 1 litre, and 5 ml of 0·04 *M* $NiSO_4$ are added and the liquid is extracted with 1 to 1·5-ml portions of toluene (for lower concn.) or carbon tetrachloride (for higher concn.) until the extracting liquid remains colourless. The colour of the combined extracts is determined photometrically, with a blue filter, or the concn. is determined by colorimetric titration. Thiophosphates, zinc, simple cyanides, and complex cyanides of Zn do not interfere; Pb, Cu and complex cyanides of Cu interfere; methods for preventing interference are given. G. S. SMITH

2326. **Colorimetric and radiometric determinations of DDT and its metabolites in resistant house-flies.** A. S. Perry, J. A. Jensen and G. W. Pearce (Dept. Health, Educ. and Welfare, Savannah, Ga., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (12), 1008–1011.—Resistant strains of house-flies are able to convert DDT into a relatively non-toxic derivative, 1:1-dichloro-2:2-di(*p*-chlorophenyl)ethylene (DDE). Quantitative studies of the products of DDT metabolism in resistant-fly strains were made with benzene soln. of ^{14}C-labelled DDT. Examination of the ether-soluble portion of the excreta by the Schechter-Haller method, and also by radioassay, shows that the only significant product is DDE. The total recovery of DDT and DDE was within the range of experimental error, except in flies held for 10 days after application of the insecticide, when losses of DDT of ≃ 14 per cent. were recorded. This is probably due to incomplete extraction of the DDT from the dehydrated flies. H. B. HEATH

Agriculture and Plant Biochemistry

2327. **Determination of plant acids by ion-exchange chromatography. I. Percuprimetric determination of tartaric acid in the presence of oxalic acid.** N. Velikonja (Inst. Agric. Chem., Univ. Zagreb, Yugoslavia). *Arhiv Kem.*, 1955, **27** (4), 161–166.—Tartaric acid is estimated in chromatographic eluates containing also oxalic, citric and malic acids. Oxalic acid is not separated from tartaric acid by chromatography on Dowex 1-X10. *Procedure*—Potassium cupri-periodate, $K_7[Cu(IO_6)_2]$, (20 to 40 ml of 0·01 *N*) (**I**) (Beck, *Brit. Abstr. C*, 1951, 397) is placed in a 100-ml flask and an aliquot of the tartaric acid solution is added and allowed to stand for 5 to 10 min. at room temp. The excess of **I** is titrated with standard arsenite to a blue end-point. Towards the end of the titration it is necessary to wait for 20 to 30 sec. between additions of arsenite. A satisfactory comparison is made between the visual and potentiometric end-points. E. J. H. BIRCH

2328. **The analysis of chlorophyll preparations.** M. Strell, A. Kalojanoff and F. Zuther (Tech. Hochschule, Munich, Germany). *Arzneimittel-Forsch.*, 1955, **5** (11), 640–642.—Four commercial samples of water-soluble chlorophyll were examined. After removal of copper by acid treatment, and of insoluble matter, the chlorophyll derivatives were fractionated by extraction from ether with graded concentrations of HCl. The fractions, after further similar purification, and in some cases after chromatography, were examined chemically and spectroscopically. No derivatives of chlorophyll-*b* were isolated. Chlorin-e_6, the primary product of hydrolysis of chlorophyll-*a*, was in each case accompanied by a greater amount of a mixture of derivatives resulting from further reactions involving oxidation and decarboxylation. Isomerisation to the corresponding porphyrin derivatives had also occurred in three of the samples, but not in the fourth. All these materials were presumably present in the original samples mainly as copper complexes. P. S. Stross

2329. **Total and radioactive phosphorus determination in small plant samples using the gravimetric method of Lorenz.** K. Strzemieński. Appendix, R. M. Williams (D.S.I.R., Wellington, N.Z.). *N.Z. J. Sci. Tech., B*, 1955, **37**, 243–257.—A method for determining total and radioactive P in the course of tracer experiments on small plant samples is described. Total P is determined, after digestion with $HClO_4$ - HNO_3, by the Lorenz gravimetric method, in which a sample soln. containing $\geq$ 50 mg of P_2O_5 is boiled, ammonium molybdate and HNO_3 soln. are added rapidly, the mixture is allowed to settle, is agitated and then allowed to stand for 2 to 18 hr. (if $<$ 3 mg of P_2O_5, 12 to 18 hr.). The ppt. is filtered off in a Gooch crucible, washed several times with 2 per cent. aq. NH_4NO_3, then with alcohol, and finally with acetone, and dried in a vacuum-desiccator for $\leq$ 30 min. The radioactivity is measured after dissolution of the ppt. in aq. NH_3 and conversion of the molybdophosphate into $MgNH_4PO_4$. The method enables both estimations to be carried out on the same sample. Self-absorption corrections are eliminated by equalising the amount of P before radioactivity measurement. In an appendix, a method is described for estimating the technical error originating from experimental procedures, as distinct from the error caused by random fluctuations in radioactivity. S.C.I. Abstr.

2330. **Flame-photometric determination of potassium and sodium in hay and other plant materials.** W. Oelschläger (Inst. for Animal Nutrition, Agric. High School, Stuttgart-Hohenheim). *Z. anal. Chem.*, 1956, **149** (3), 190–195.—In the flame-photometric determination of K and Na in hay-ash, K is determined first because no other elements appear to interfere. For the determination of Na, Ca must be removed and a correction applied (from calibration curves) for the content of K. A coal-gas flame is used to avoid excitation of other elements. J. P. Stern

2331. **Estimation of K, Ca, Mg and Na in vegetable ash. Estimation of total nitrogen by semi-micro distillation.** E. Bovay (Station Fédérale de Chim. Agric., Lausanne, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (6), 540–568.—In the flame-photometric methods described the solutions are prepared by ashing the sample (10 g) for 15 hr. at 550° C. The ash is taken up in 3 *N* HCl (25 ml), the mixture is boiled for 10 min., cooled and filtered, and the filtrate is made up to 200 ml with H_2O purified by an ion-exchange resin. The determination of K and Na is not influenced by the elements normally present in plant ash, but the determination of Mg and Ca is markedly affected by PO_4''', SO_4'', Si and Fe. The preparation of standard curves for Mg and Ca, with compensating soln. which have compositions resembling as far as possible those of plant ash, is described. In the semi-micro method for the estimation of N, the conventional steam trap is replaced by a short fractionating column to enable a more rapid distillation of the ammonia. W. H. Parr

2332. **Sampling variations in the concentrations of elements in soils.** R. M. McKenzie (Soil Div., C.S.I.R.O., Adelaide). *Aust. J. Agric. Res.*, 1955, **6** (5), 699–706.—The sampling error, in terms of the coefficient of variation, in a spectrographic determination of the concn. of Cu (14 to 26), Mg (9000 to 18,000), Ga (7 to 15), V (94 to 200), Mo (1·5 to 3·5) and Mn (600 to 1000 p.p.m.) in a supposedly uniform soil is found to be $\simeq$ 10 per cent. for each of these trace elements. This figure is based on 68 samples taken on an 8·5-inch grid over a plot (8 ft. $\times$ 3½ ft.). There is more correlation between the concn. of pairs of elements than can be explained wholly by the method of determination. The total error for a triplicate analysis of a single soil sample taken in the manner described is, as a measure of average level for the whole area, 12·8 per cent.; of this, 8·0 per cent. represents spectrographic error. B. J. Walby

2333. **Mercurimetric method of micro-determination of chloride ion in soil.** L. N. Lapin and R. Kh. Zamanov. *Pochvovedenie*, 1954, (11), 80–84; *Ref. Zhur., Khim.*, 1955, Abstr. No. 23,970.—One part of the soil is shaken for 5 min. with 5 parts of water, and 5 ml of the extract are mixed with 10 ml of 96 per cent. ethanol. Any cloudiness is disregarded. Two drops of 1 per cent. alcoholic diphenylcarbazide solution are added, followed by *N* HNO_3 added dropwise to decolorise, and the solution is titrated with 0·1 *N* or 0·01 *N* $Hg(NO_3)_2$ to a pale-violet end-point. The method is more accurate than that of Mohr. A micro-burette without stop-cock is described. G. S. Smith

2334. **Leaching of some fission products from soil.** B. Kahn (Oak Ridge Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 216–218.—The radiochemical determination of radionuclides adsorbed on soil can be simply effected by washing the sample (5 g) with suitable vol. and concn. of boiling HNO_3, H_2SO_4 and oxalic acid, respectively, removing non-radioactive ions (by modification of standard procedures) and then separating the radionuclides by radiochemical methods. The preferred leaching solutions are: 9 *M* H_2SO_4 for ^{137}Cs and ^{106}Ru, *M* HNO_3 for ^{90}Sr, ^{90}Y and ^{144}Ce, and 0·5 *M* oxalic acid with *M* HCl for ^{95}Zr and ^{95}Nb, three washings of 20 ml each being effective. When removing Ru, 0·5 g of $KMnO_4$ is added to the acid, and the RuO_4 is separated from the soln. by distillation. Recovery of each element is $\simeq$ 99 per cent. W. J. Baker

2335. **Holocellulose and the summative analysis of forages.** R. E. Ely and L. A. Moore (Dairy Husbandry Research Branch, U.S. Dept. Agric., Beltsville, Md., U.S.A.). *J. Anim. Sci.*, 1955, **14**,

718–724.—In the analysis of forages (hay, silage, straw) the crude fibre + N-free extractive component is largely accounted for by determination of lignin + holocellulose (as cellulose + hemicellulose). It is suggested that the analysis of such materials should comprise determinations of ash, protein, lignin, holocellulose, hot-water extractives and alcohol - benzene extractives. A. G. POLLARD

2336. **Determination of 6-ethoxy-1:2-dihydro-2:2:4-trimethylquinoline in biological materials.** E. M. Bickoff, J. Guggolz, A. L. Livingston and C. R. Thompson (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (3), 376–378.—The method is fluorimetric. The 6-ethoxy-1:2-dihydro-2:2:4-trimethylquinoline (**I**), an antioxidant for carotene, is separated from the biological material by extracting first into acetone and then into *iso*octane; the fluorescence of this soln. is then measured. The soln. is then treated with $KMnO_4$ soln., which completely quenches the fluorescence due to **I**. The difference in readings gives the **I** content. Minor modifications are made according to the material analysed. The method is capable of detecting 0·01 p.p.m. of **I**.
G. P. COOK

2337. **Analysis of sulphur products.** J. R. Gray (Burt, Boulton & Haywood Ltd., Belvedere, Kent, England). *J. Sci. Food Agric.*, 1956, **7** (1), 3–7.—The methods of analysis to evaluate the properties of S in the form of dusts and sprays are discussed, including methods of assessing particle size, bulk density, dustability and retention; methods of determining the amount of S present are considered and that of Goodwin - Martin (*J. Agric. Sci.*, 1925, **15**, 96) is recommended. S.C.I. ABSTR.

2338. **Toxicological detection of the plant-protection agent Systox.** W. Völksen (Städt Krankenhaus., Nordstatt, Germany). *Dtsch. ApothZtg*, 1955, **95** (36), 865–866.—Identification tests for OO-diethyl O-ethylthioethyl thiophosphate (**I**), the chief active constituent of Systox, based on the affinity of thioethers to form insol. sulphonium compounds with metal salts, halogens and halogen-alkyls, are discussed. Turbidity reactions with (*a*) Mayer's reagent, (*b*) gold chloride, in aq. dilutions of **I** down to 1 in 50,000 and 1 in 20,000, respectively, and colour reactions with (*c*) sodium nitroprusside, (*d*) molybdophosphate or Folin - Ciocalteu's reagent of aq. dilutions of **I** down to 1 in 5000 and 1 in 100,000, respectively, are described. The above reactions were successfully applied to the detection of Systox in the stomach contents in a fatal case of poisoning.
S.C.I. ABSTR.

2339. **Quantitative determination of some dialkyldithiophosphoric acids by means of colorimetric determination of their nickel salts.** M. Masoero and M. Perini (Antiparasite Lab., Società Montecatini, Novara, Italy). *Chim. e Ind.*, 1955, **37** (12), 945–949.—Absorption spectra in the visible region are given for nickel salts of some dialkyldithiophosphoric acids in benzene solution; conditions for colorimetric qualitative analysis have been determined. The method is applicable to the titration of crude industrial acids, especially for dimethyl- and diethyl-dithiophosphoric acids. Experimental procedure is described for the technique, which has an accuracy within $\simeq$1 per cent.
C. A. FINCH

2340. **Analysis of coal-tar fungicides.** G. V. Coles (P.O. Box 227, Kampala, Uganda). *J. Sci. Food Agric.*, 1956, **7** (1), 11–17.—The difficulties encountered in applying an existing standard method of analysis of coal-tar prep. to the separation of the constituents of certain fungicides used for treatment of rubber-tree disease are discussed. The scheme of analysis involves the preliminary removal of water and formulating materials by using simple apparatus, and is followed by countercurrent extractions. Details are given of the procedure and the extractor used is illustrated. A sample of $\simeq$25 g of water-free material is used, with benzene as the extracting liquid. S.C.I. ABSTR.

See also Abstracts 2142, 2241.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2341. **Self-indicating magneto-electric balances.** M. A. Gurevich and K. P. Malyus-Malitskii. *Zhur. Teckn. Fiz.*, 1954, **24** (9), 1724–1728; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,554.—Two self-indicating balances are described. The first records small changes of weight of relatively heavy objects with time. The second gives not only the total change in weight but small sections of the process on a magnified scale. Calibrations of the balances are practically independent of the weight of the sample over a wide range of changes in weight. A balance of this type can measure a change of weight of 10^{-6} g in a sample weight of 1 g. G. S. SMITH

2342. **Use of quartz sorption-balances for studying the sorption capacity of coal at high pressures.** V. V. Khodot and M. F. Yanovskaya. *Doklady Akad. Nauk, SSSR*, 1954, **97** (5), 879–881; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,581.—The apparatus is designed to test the sorption properties of coal over the pressure range of 10^3 mm of Hg to 50 atm. It consists of a thick-walled cylinder of transparent plastic inside a steel cylinder with a viewing window, fitted with a valve for inlet of gas under high pressure and a vacuum valve for evacuation of the system and degasification of samples of coal. Inside is hung a quartz spring with a sample container. A battery of 10 to 12 such vessels is connected to a single vacuum line and a single source of compressed gas. G. S. SMITH

2343. **Anhydrous hydrogen chloride generator.** H. Taniguchi and G. J. Janz (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 287–288.—An all-glass apparatus, in which the spent reaction mixture can be quickly siphoned off and replaced by a new charge, is described and illustrated. The mixture used is H_2SO_4 and either conc. HCl or solid NaCl (5 to 50 g). W. J. BAKER

2344. **Inexpensive micro-titrator.** K. A. Allen (Oak Ridge Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 277.—The micro-burette shown consists of a Teflon piston (with expanded end to ensure liquid-tightness) fitting a precision-bore glass tube, which is connected to a capillary tip by a taper-joint and is fixed rigidly to a micrometer. The piston is operated through the micrometer handle, vol. (0·2 ml) equiv. to a piston travel

of 0·1 in. being read to ± 0·1 per cent. For very small vol. (piston travel 0·006 in.), temp. control to ± 0·05° C is necessary, namely, a water-jacket around the glass tube. W. J. BAKER

2345. **Heated vacuum-desiccator.** F. T. Wadsworth (American Oil Co., Texas City, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 287.—The vacuum-desiccator described is intended for the rapid drying or removal of very small amounts of solvent from a substance. The porcelain plate is replaced by a glass heating plate (500 W per sq. ft. at 110 V) supported so as to minimise heat transfer to the desiccator. Two holes are drilled through the wall for the electrical leads. Temp. control is through the applied voltage. W. J. BAKER

2346. **Comparative tests of moisture ovens.** Institute of Brewing: Analysis Committee (33 Clarges St., London). *J. Inst. Brewing*, 1956, **62** (1), 7–9.—Samples of a well-mixed ground malt were submitted to 16 laboratories for moisture determinations. Results show that by using a boiling-water oven (Institute of Brewing pattern) good agreement was obtained between laboratories; the average figure for moisture was 3·59 per cent. and the standard error for duplicates was ± 0·05 per cent. When electrically heated ovens were used only poor agreement was obtained between laboratories. Assessment of the ovens was made by the copper sulphate test. The requirement is that pure $CuSO_4.5H_2O$ (5 g), passing a 16-mesh sieve, should lose 21 to 25 per cent. of its weight in 30 min. in the pre-heated oven. G. H. BAKER

2347. **Semi-micro digestion with nitric-sulphuric acid.** J. Pien. *Ann. Falsif.*, 1955, **48**, 420–421.—An apparatus for rapid macro-digestion of organic material with a mixture of HNO_3 and H_2SO_4 (*Anal. Abstr.*, 1955, **2**, 504) can be advantageously adapted for use with quantities of about a gram or a few decigrams. A 100-ml reaction flask is used and fumes reaching a reflux condenser at the top of the apparatus run back to a chamber from which return to the reaction flask is controlled by a tap. A tap-funnel beside the chamber permits the addition of more acid if necessary. The apparatus is made of glass with ground glass joints. Advantages claimed are the short time of working (less than one-sixth of that of the classical method), economy of reagents, prevention of adventitious contamination and control of noxious fumes. D. G. FORBES

2348. **Apparatus for molecular filtration.** C. F. Hiskey and A. N. Kivert (Internat. Biochem. Corp., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 246–247.—The mol. filter described and illustrated consists of a tubular cellulosic membrane (10 to 15 ft. long, 0·25 in. inside diam.) supported throughout its length by cotton braid, the whole being coiled and encased in a nylon bag. There are plastic valves at inlet and outlet ends of the tube, loading being effected by connecting the stainless-steel reservoir to one of these valves. Filtration rates up to 500 ml per hr. at 100 lb pressure are attainable, reactivation of the plugged membrane being effected periodically by washing through the tube with water. The filter can be used for the quant. removal of proteins from extracts, beers, etc., removal of bacterial pyrogens from clinical soln., of hydrophobic phases from aq. soln., and for the initial concn. of dil. soln. of proteins, hormones, viruses, etc. W. J. BAKER

2349. **Packing adsorbents in chromatographic columns.** W. L. Rankin (Jennie Edmunds Memorial Hosp., Council Bluffs, Iowa, U.S.A.). *Anal. Chem.*, 1956, **28** (2), 288.—A method for obtaining uniform packing of adsorbents in chromatographic columns is described. G. P. COOK

2350. **Some improvements in the technique of paper chromatography.** E. Steinegger and F. Ochsner (Pharm. Inst., Univ. Bern, Switzerland). *Pharm. Acta Helv.*, 1955, **30** (9), 345–350.—A number of detailed improvements are described. Impregnation of papers with a lipophilic stationary phase is best done by dissolving the substance in a volatile solvent; acetone was found the most suitable. It is important, when applying the material to be chromatographed to the paper, to do this in a solvent readily miscible with the stationary phase. If this is not possible the paper should be dipped after the spot has been applied. A simple apparatus for eluting the material from paper with the minimum quantity of liquid is described. Details are given of techniques found useful for the preparation of cellulose columns to be used for preparative chromatography. P. S. STROSS

2351. **Chromatographic chamber for simultaneous preparation of many paper chromatograms.** I. R. Hunter, D. F. Houston and H. S. Owens (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 283–284.—A chromatographic tank was devised, by modification of a commercial photographic developing tank, to accommodate up to 60 chromatographic papers 9 in. × 9 in. G. P. COOK

2352. **A semi-automatic apparatus for maintaining solvents with changing polarity in chromatographic columns.** M. R. Sahasrabudhe and S. L. Tuckey (Univ. Illinois, U.S.A.). *J. Dairy Sci.*, 1955, **38** (12), 1392.—With the apparatus described, a solvent of gradually changing polarity can be passed under pressure through a chromatograph column, while maintaining a constant head of liquid over the column. W. H. C. SHAW

2353. **Simple large-volume fraction collector for column chromatography.** V. Ginsburg (Univ. Calif., Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 279–280.—The outlet of the column is connected to a slightly sloping manifold to which are connected several collection flasks. When the first flask is filled the eluate rises into an exhaust tube until the pressure head equals that of the incoming eluate. The eluate then enters the second flask and the process is repeated. G. P. COOK

2354. **Trough for use in descending paper chromatography.** J. F. Thompson and M. V. Marion (Agric. Res. Serv., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 288.—A borosilicate-glass trough for use in descending paper chromatography is described. G. P. COOK

2355. **Van Slyke manometric apparatus modified for determination of free amino nitrogen in solid samples.** K. T. Williams and M. C. Long (Agric. Res. Service, U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 144.—The Van Slyke apparatus (*J. Biol. Chem.*, 1929, **83**, 425) for the determination of amino nitrogen was modified to take solid samples such as wool, potato granules, poultry meat and feathers. G. P. COOK

2356. **Application of vapour-phase chromatography in the gas-analytical field.** F. van de Craats (Konink. Shell-Lab., Amsterdam, Netherlands). *Anal. Chim. Acta*, 1956, **14** (2), 136–149.—The general principles of gas - solid chromatography and gas - liquid partition chromatography are discussed. The practice of the latter is considered in relation particularly to the separation of the lower hydrocarbons, saturated and unsaturated. Some detail is given of the methods employed for determining the separated gases in the stripper gas. Continuous thermal conductivity measurement is used when the number of components is limited, or when only one component is to be determined in a complex mixture. When the mixture has many components the stripper gas (CO_2) is absorbed, the gases are passed into an evacuated receiver and the pressure increases in the receiver are measured automatically.
W. C. JOHNSON

2357. **Sealed capillary viscometer.** R. Z. Suleĭmanova. *Zhur. Fiz. Khim.*, 1954, **28** (10), 1820–1824; *Ref. Zhur., Khim.*, 1955, Abstr. No. 26,585.—The viscometer consists of a U-tube capillary, 190 mm long, both limbs of which are joined at the top leaving an opening for filling and sealing. One limb has two marks 40 mm apart. The viscometer is half filled with the liquid under test and the inlet is then fused. It is held immersed in a thermostat attached to a rotating device so that its axis of symmetry is parallel to the horizontal axis of rotation of the device. The time for the meniscus to pass between the marks is measured while the viscometer is turned through a definite angle. The accuracy of measurement is $\pm$ 2 per cent.
G. S. SMITH

2358. **Apparatus for automatic determination of gel time.** J. S. Billheimer and R. Parrette (Aerojet-General Corp., Azusa, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 272–273.—The apparatus periodically dispenses a glass bead to the surface of a polymerisation sample immersed in a constant-temp. bath. While the sample is fluid the beads sink to the bottom and after the gel has formed the subsequent beads are retained on the top surface of the sample. The gel time is indicated by the no. of beads in the bottom of the gelled mass. The standard deviation was $\pm$ 2·3 per cent. of a mean of 4·8 hr.
G. P. COOK

See also Abstracts 1971, 1976.

Optical

2359. **A valuable auxiliary to microchemical analysis: the microscope.** S. Stoll. *Chim. Anal.*, 1955, **37** (12), 409–415.—A review is given of the use of the microscope for the determination of emission spectra, absorption spectra, molecular weights, and melting- and boiling-points. (23 references.)
C. A. SLATER

2360. **Colour comparator for determination of water in Cellophane.** H. A. Scopp and C. P. Evans (Olin Mathieson Chemical Corp., New Haven, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (1), 143–144.—A simple apparatus consists of a twin-compartment box fitted with a central vertical partition, on one side of which is the titration vessel (16-oz bottle) and on the other a glass filter (670 mμ). Behind the apparatus is a source of light. The titration vessel, supported on a magnetic stirring apparatus, is fitted with a three-holed rubber bung, which carries (*i*) a drying-reagent tube, (*ii*) the burette, and (*iii*) a removable rubber stopper for addition of the sample. The sample is titrated with Karl Fischer reagent against two drops of methylene blue indicator (0·1 per cent. in pyridine) until the colour of the two halves of the front screen match. Materials other than Cellophane have been successfully analysed with this apparatus, *e.g.*, benzene, polyethylene and paper. Certain substances, such as $BaCl_2$ and Na tartrate, cloud the solvent and tend to mask the end-point. Results are claimed to be within $\pm$ 1·7 per cent. of the H_2O content.
D. G. HIGGS

2361. **Instrumentation and principles of flame spectrometry. Multichannel flame spectrometer.** B. L. Vallee and M. Margoshes (Harvard Med. School, Boston, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 175–179.—The instrument described determines simultaneously the elements Na, K, Mg, Ca and Sr; it comprises an oxy-hydrogen burner, grating monochromator, photomultiplier detectors with associated power supplies, amplifier and meters. As little as 0·002 μg of Na per 1 ml of H_2O is readily detected and the calibration curves cover a 1000-fold range of concn. for each element. The precision claimed compares favourably with that for other flame photometers.
D. G. HIGGS

2362. **Instrumentation and principles of flame spectrometry. Effect of extraneous ions in simultaneous determination of five elements.** M. Margoshes and B. L. Vallee (Harvard Med. School, Boston, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 180–184.—The effects of extraneous ions on flame-spectrometric or -photometric analysis have been studied with the multichannel flame-spectrophotometer. It has been shown that extraneous cations produce a heterogeneous background radiation but have no effect on the monochromator emission intensity measured above background. The elements Na, K and Mg emit radiation at 5498 A (CaO bandhead) with an absolute background intensity different for each element, but all three background curves run parallel to the calibration curve for Ca. The anions PO_4''', $(C_2O_4)''$, SO_4'' and $(AlO_2)'''$, at concn. $\gtrsim$ Ca concn., sharply decrease the CaO emission to a certain critical stage, beyond which, further increase in anion concn. produces no further change in emission. Similarly, the emission of Sr is affected by $(AlO_2)'''$, PO_4''' and SO_4'', but not by $(C_2O_4)''$. Correction for background is automatically applied with this instrument. Methods of avoiding anion interferences are briefly discussed.
D. G. HIGGS

2363. **Spectrochemical analysis with time-resolved spark spectra.** Á. Bardócz and F. Varsányi (Central Res. Inst. Physics, Hungarian Acad. Sci., Budapest, Hungary). *Nature*, 1956, **177**, 222–223.—An optical arrangement for almost completely eliminating the background from high-voltage spark spectra is described and illustrated. It includes an electronically controlled spark source and a concave rotating mirror, the movement of which is synchronised accurately with the initiation of the separate spark discharges. The spectrum is detected photoelectrically or photographically. The advantages of the procedure in spectrochemical analysis are indicated by photographs and density curves for the spark spectrum of an alloy of Al - 0·01 per cent.

Cu. By coating one side of the mirror with Al and the other with black paper, only that light emitted by the spark between 29 and 54 microsec. is used, thus increasing the ratio of line to background density. W. J. BAKER

2364. **Semi-quantitative spectrochemical analysis using Spex standards.** A. J. Mitteldorf and D. O. Landon (Spex Industries Inc., Queens Village, N.Y., U.S.A.). *Applied Spectroscopy*, 1956, **10** (1), 12–14.—A method is described for the analysis of a wide range of organic and inorganic materials which is capable of an accuracy of at least ± 30 per cent. for any detectable element. Standards are prepared by mixing together compounds of 43 common elements and then mixing with graphite or other pure material to give concn. of 0·1, 0·01, 0·001 and 0·0001 per cent. of each element. The samples (after ashing if necessary) are mixed with the same pure base material in ratios of 1:9, 1:99 or 1:999 if elements in concn. > 50 per cent. are being determined. Diluted samples and standards are loaded into cratered graphite electrodes and burned to completion in a d.c. arc of 8 to 10 amp. The spectra of samples and standards are first compared visually on a microphotometer and then further by taking transmittance readings and plotting reading *vs.* percentage concn. of standards to give an interpolated result for the samples.
K. A. PROCTOR

2365. **New spectrometer slit mechanism.** H. M. Crosswhite and W. G. Fastie (John Hopkins Univ., Baltimore, Md., U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (2), 110–115.—In this new type of spectrometer slit, the jaws are connected to opposite sides of a flexible steel ring, which is then distorted under load to obtain the required slit opening. In applications requiring circular slits, one edge of the ring is used as one jaw of the slit. For high resolution applications, slits of this type may be made which are 25 mm long, a few microns wide and reproducible in width to a few tenths of a micron.
B. S. COOPER

2366. **Adaptation of existing potassium bromide disc press for microdisc pressing *in vacuo*.** R. A. Pickering (Argonne Cancer Res. Hosp., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 280.—The adaptation reported in this note involves mounting a press in an evacuation chamber fitted with an O-ring seal, a rubber seal around the plunger and a side arm to the vacuum system. Discs of KBr, pressed directly into a steel sleeve for ease of handling and mounting, are 6 mm in diam. and pressed between hardened surfaces that have been polished to optical flatness. D. G. HIGGS

2367. **Current sources and controllers for the d.c. arc.** G. H. Fetterley (Norton Co., Niagara Falls, Ontario, Canada). *Applied Spectroscopy*, 1955, **9** (3), 118–130.—Published information on d.c. arc sources is discussed and attention is drawn to an electronic rectifier described by Fetterley and Hazel (*J. Opt. Soc. Amer.*, 1950, **40**, 76), which delivers up to 45 amp. at 150 V from a 3-phase 115-V supply. The equipment is claimed to be compact and light in weight, of low cost and to require negligible maintenance. P. T. BEALE

2368. **An important application of ultra-violet absorption spectrophotometry.** L. Láng and É. Falta (Centr. Phys. Res. Inst., Hung. Acad. Sci., Budapest). *Magyar Kém. Foly.*, 1956, **62** (2), 66–67.—It was found that the ultra-violet spectrum of phenanthrene, as recorded in the literature, also shows absorption bands of anthracene and fluorene, although the m.p. and the micro-analytical figures were fairly accurate. Thus it is suggested that besides the m.p. and micro-analysis, the ultra-violet absorption should also be used to identify a compound. A. G. PETO

2369. **A new method for the quantitative evaluation of ultra-violet spectroscopic photographs.** T. Bálint (Hung. Petroleum and Nat. Gas Exp. Inst., Veszprém). *Magyar Kém. Foly.*, 1956, **62** (1), 3–6.—A simple and rapid method is described for u.v. absorption spectroscopy, for which neither a voltage stabiliser nor a divided beam is required. The errors, caused by the change in intensity of the hydrogen lamp, are eliminated by a correction calculated from the degree of darkening measured at certain reference wavelengths. A simple apparatus can be used, with a very narrow slit and a short exposure. The method is particularly suitable for serial analyses containing one or more components. For a mixture of the three cresols, the accuracy was within ± 1·9 per cent. A. G. PETO

2370. **Infra-red analysis—a progress report on an advancing method.** N. Wright. *Applied Spectroscopy*, 1955, **9** (3), 105–118.—The development of instruments and applications of i.r. analysis from 1937 to the present day are surveyed. Current needs are listed as follows—(1) a cell-window material, with high transmittancy to 15 μ or beyond, water insolubility and good mechanical strength, to replace rock-salt; (2) better resolving power, which could be provided by gratings; and (3) higher precision in resetting to specified wavelengths, which again could be given by the use of gratings or by the double-beam differential method.
P. T. BEALE

2371. **Continuous-flow infra-red gas analyser employing interference filters.** J. L. Parsons, M. J. Irland and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (3), 164–166.—A single-beam filter photometer, with particular application to the determination of hydrocarbons in automobile-engine exhaust gases, is described. The source of radiation is a nickel - chromium alloy ribbon-filament wound on a former to provide a source area of approx. 1 sq. in.; this normally operates at 450° K, consuming 40 watts at 12 V. Radiation from the source passes through an aluminium tube, 20 in. long, 1 in. in diam., which serves both as gas cell and optical collimator. A combination interference filter incorporating both band pass and long wavelength pass elements isolates radiation of 3·43 μ with peak transmission 70 per cent. and half-band width of 0·15 μ. The detector is a compensated vacuum thermopile of sensitivity 2 μV per μW from which the signal is fed to a potentiometer circuit.
B. S. COOPER

2372. **Simple Raman apparatus and procedure for the analysis of hydrocarbon mixtures.** P. Szolcsányi (Phys.-Chem. Dept., Univ. Chem. Ind., Veszprém, Hungary). *Magyar Kém. Foly.*, 1956, **62** (1), 7–11.—Details are given of a new, simple Raman apparatus, which was developed on the basis of the author's theory of Raman sources. The 4358-A line of a directly water-cooled 450-W

mercury-vapour lamp is used for excitation. The irradiator is a cylindrical mirror; the lamp and the cell are placed along its diameter, at a distance of half a radius from the vertical axis. The windowless cell has a capacity of 5 ml; the light passes out through the free liquid surface. There is no meniscus, as the upper part of the cell is conical. The spectrum is measured with a recording photometer. A semi-quant. analysis can be made from the height of the maxima, measured by the baseline method. The method is much quicker than the usual procedures, and its accuracy is sufficient for the purpose required. A. G. PETO

See also Abstracts 1989, 2058, 2197.

Thermal

2373. **Performance requirements for electrically heated laboratory drying ovens.** British Standards Institution (B.S. 2648: 1955, 12 pp.) (2 Park St., London).—The standard covers the type of oven used for the determination of moisture by drying within the range 95° to 110° C, and adjustable within 0·5° C of any desired temp. within that range; the ovens have an internal space of 1 to 3 cu. ft. and are ventilated by convection; they may be fitted with internal fans; vacuum ovens or forced-draught ovens are not included. The temp. variation measured at the same time at different positions in the oven must not exceed 2·5° C; the temp. fluctuation at any point must not exceed 1·0° C over a period of 30 min. Standards are also given for temp. drift, reproducibility of temp., time of temp. recovery, temp. overshoot and ventilation rate. N. E.

Electrical

2374. **High-frequency analysis. XI. Measurement of dielectric constant, dielectric loss and conductivity and their application.** Morizo Ishidate and Yukichi Kamura (Medical Faculty, Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1954, **74** (8), 827–830.—For the measurement of dielectric constant of an electrolytic soln., a bridge circuit and a cell were devised. The cell comprises two concentric glass cylinders, the outer surfaces of which are covered with thin films of metal. The sample soln. is placed between the cylinders. When acid-base titrations are carried out with this apparatus, satisfactory results are obtained over a wide range of concn. The change in capacity is theoretically discussed with the aid of an equivalent circuit. K. SAITO

2375. **RC-Titration. A new method for determining conductivity without electrodes.** R. Huber and K. Cruse (Phys. Chem. Inst., Clausthal, Germany). *Angew. Chem.*, 1956, **68** (5), 178–181.—Techniques for measuring conductivity with electrodes which have no galvanic contact with the solution under examination are discussed and the theory covering RC-titration is detailed. In the RC-titrimeter the cells are the same as used in other high-frequency titrations without electrodes; the cells are in one branch of a Wien-bridge in the RC-generator; the frequency in the RC-generator is proportional to the conductivity of the solution. The advantage of the new method is that, without alteration to the titrimeter and with the same cell, it permits the determination of conductivities ranging over several powers of ten. The accuracy of the method depends on the frequency stability attained and on the accuracy of the frequency determination. J. P. STERN

2376. **A laboratory electrodialyser and desalter.** T. Wood (Bovril Ltd., 148–166 Old St., London). *Biochem. J.*, 1956, **62** (4), 611–613.—A simple Perspex electrodialysis cell is described. It involves the use of Permaplex ion-exchange membranes or collodion membranes, and can be used for the desalting or fractionation of complex mixtures by electrodialysis. J. N. ASHLEY

2377. **An apparatus for high-tension paper electrophoresis.** G. Werner (Forschungsinst., Säckingen, Germany). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (5), 613–626.—Details are given of an electrophoresis apparatus with a voltage of 10,000 and a migration up to 1 metre, and a method is described for applying the soln. of a substance to paper which ensures uniform and reproducible wetting of exceptionally long strips. The method has been successfully employed for the separation of amino acids and peptides, nucleotides and other org. phosphoric acid derivatives, boric acid complexes of sugars, amines, carboxylic acids, and purines. P. HAAS

2378. **Zone electrophoresis on an inert support. III. Preparative electrophoresis in massive inert support.** R. Munier (Inst. Pasteur, Paris). *Chim. Anal.*, 1955, **37** (10), 340–346.—Preparative electrophoresis in inert supports is considered under three headings—electrophoresis in slabs, in horizontal tubes and in vertical tubes. Examples of the various methods are given. Whilst not possessing the precision nor the rapidity of "frontal" electrophoresis, which is suitable for qual. micro-analysis, electrophoresis in inert supports is an excellent technique for the purification of ionisable material. As most of the difficulties to be encountered are linked with the adsorptive power of the support, efforts should be made to produce a support as inert as possible. J. H. WATON

2379. **Convenient starch electrophoresis apparatus.** K. Paigen (Univ. Calif., Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 284–286.—A simple and convenient apparatus for electrophoresis with starch as the supporting medium is described. It possesses a number of advantages over the usual wax paper and glass arrangement. G. P. COOK

See also Abstracts 1977, 1984, 2181, 2182, 2230, 2231, 2242.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher, -e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline, crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_{λ}^{t}
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_{\lambda}^{t}$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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